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**Processing and Advanced Characterization of
Pure and Ln-Doped UO_2 Pellets Fabricated by
Spark Plasma Sintering**

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Processing and Advanced Characterization of Pure and Ln-Doped UO_2 Pellets Fabricated by Spark Plasma Sintering

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Abstract

This thesis investigates how spark plasma sintering (SPS) parameters, powder characteristics, and lanthanide doping influence the densification and structural response of UO_2 -based nuclear fuel materials. First, a systematic pressure–temperature sintering map was established for pure UO_2 using a low surface area starting powder. Densification increased with temperature and pressure but reached a plateau at approximately 93–94% of theoretical density. The results indicate a transition from pressure-assisted particle rearrangement to diffusion-limited pore elimination, with the final density strongly influenced by the characteristics of the starting powder. Second, five UO_2 -based materials containing 1 wt% La, Ce, Pr, Nd, or Gd were synthesized by co-precipitation and consolidated by SPS. Relative densities of 96–98% were achieved. Synchrotron high-resolution powder diffraction confirmed retention of the fluorite structure without detectable secondary crystalline phases and revealed systematic changes in lattice parameter. Agreement with a hard-sphere model supports substitutional incorporation of the lanthanides and indicates that the lattice response is primarily governed by cation size and charge compensation. ICP–MS and laser ablation ICP–MS further confirmed compositions close to the targets and no pronounced large-scale compositional variation within the analysed regions. Together, the results demonstrate that control of powder characteristics, precursor chemistry, and SPS conditions is essential for producing dense and structurally well-defined surrogate nuclear fuel materials.

Keywords: uranium dioxide, UO_2 , spark plasma sintering, lanthanides, simfuel.

List of Publications

This thesis is based on the following publications:

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Synthesis and structural characterization of single lanthanide-doped UO_2 prepared by co-precipitation and spark plasma sintering.

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Publication II

Densification limits of low surface area UO_2 during spark plasma sintering.

Georgios Zagoraios, Hannah Kreutzer, Elisa Fernandez Acguedi, Christos Andrikopoulos, Christian Ekberg, and Marcus Hedberg.

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1

Introduction

Electricity is essential in modern society and supports industry, transport, communication, and everyday life. Global electricity demand continues to rise as populations grow and technological systems expand. At the same time, reducing greenhouse gas emissions from energy production has become a central objective in efforts to mitigate climate change. These parallel challenges have intensified the need for large-scale, reliable, and low-carbon electricity generation technologies.

Nuclear power provides stable electricity with very low direct carbon emissions and therefore remains an important component of the global energy system. Hundreds of commercial reactors operate worldwide, contributing a significant fraction of total electricity production. In Sweden, nuclear energy has long played a central role in the national electricity supply. Despite ongoing discussions regarding safety, waste management, and long-term sustainability, continued reactor operation and future deployment strategies depend on reliable fuel performance and improved understanding of fuel behavior.

The dominant fuel used in current light-water reactors is uranium dioxide (UO_2). Its thermophysical properties, chemical stability, and irradiation response have made it the standard commercial fuel for decades [3]. Fuel performance during operation is governed not only by composition but also by density, porosity, grain structure, and defect chemistry, all of which are initially established during fabrication [4, 5]. In addition, incorporation of fission products during reactor operation modifies the crystal structure and local chemistry of the fuel matrix [6, 7].

Beyond processing considerations, the study of nuclear fuel materials, particularly after irradiation, remains experimentally challenging due to intense radiation, high toxicity, and complex chemical evolution during burnup [8, 9]. To isolate specific chemical and structural phenomena under controlled laboratory conditions, simulated fuels (simfuels) are frequently employed, in which selected fission product elements are incorporated into the UO_2 lattice [10, 11]. Among these elements, lanthanides constitute a significant fraction of the fission product inventory and are known to influence the thermophysical and structural properties of UO_2 [12, 13].

This thesis addresses two interconnected scientific objectives. The first is to determine how Spark Plasma Sintering (SPS) processing parameters and starting-powder characteristics govern the densification behaviour of pure UO_2 . SPS has attracted increasing interest for nuclear fuel fabrication because it enables rapid pressure-assisted consolidation at shorter processing times than conventional sintering routes. These characteristics make SPS a promising technique for the fabrication and study of advanced nuclear fuel materials.

The second objective is to evaluate how controlled lanthanide substitution influences the crystal structure of UO_2 when the material is fabricated under defined processing conditions. Single-lanthanide-doped UO_2 systems provide a simplified approach for isolating the structural effects of individual fission product surrogates without the complexity of multi-component irradiated fuel. To address these objectives, a systematic SPS parameter map was established for pure UO_2 , while five single-lanthanide-doped UO_2 compositions containing 1 wt% La, Ce, Pr, Nd, and Gd were synthesized by co-precipitation, consolidated by SPS, and characterized using complementary chemical, microstructural, and high-resolution structural techniques. Together, these studies examine how precursor properties, processing conditions, and chemical composition interact to control densification and lattice response in UO_2 -based nuclear fuels.

2

Background

2.1 Uranium dioxide as a nuclear fuel

Since the first controlled nuclear chain reaction in 1942, nuclear reactor technology has developed through several generations, with continuous efforts directed toward improved safety, efficiency, fuel utilization, and waste management. Early reactor systems demonstrated the feasibility of sustained energy production based on nuclear fission, while Generation II reactors became the foundation of commercial nuclear power. These include pressurized water reactors and boiling water reactors, where uranium dioxide is commonly used as the fuel material in the form of ceramic pellets.

Later Generation III and III+ systems introduced improved safety systems, enhanced containment concepts, and extended operational lifetimes. Current research on advanced nuclear energy systems increasingly focuses on Generation IV concepts and closed nuclear fuel cycles based on the recycling of plutonium and minor actinides. These approaches aim to improve fuel utilization while reducing the inventory of long-lived radioactive waste [14].

Across these reactor generations, fuel performance remains central to reactor operation. The fuel must maintain its integrity under high temperature, irradiation, and chemically demanding conditions. Nuclear fuel materials must therefore satisfy strict thermophysical, chemical, and mechanical requirements, including high melting temperature, chemical stability, compatibility with cladding materials, resistance to degradation, and dimensional stability during operation [14]. These requirements are directly connected to reactor safety margins and long-term fuel reliability [15, 16].

Among ceramic nuclear fuels, uranium dioxide (UO_2) remains the dominant material for light-water reactors. Its widespread use is related to its high melting temperature, chemical stability, compatibility with zirconium-based cladding under reducing conditions, and well-established industrial fabrication route. At the same time, UO_2 has limitations, most notably its relatively low thermal conductivity [17]. This leads to significant temperature gradients across the fuel pellet during operation, which can influence fission gas release, cracking, restructuring, and fuel-cladding interaction [3, 15]. As a result, the final density, porosity, and microstructure of the fuel pellet are important parameters for fuel performance.

The properties of UO_2 are also sensitive to oxygen stoichiometry, irradiation, and chemical defects [18]. Small changes in composition can affect structural and thermophysical properties, making accurate characterization important when evaluating processed or simulated fuel. Precise lattice parameter measurements of stoichiomet-

ric UO_2 provide an important reference point for assessing structural changes in UO_2 -based fuels [19].

Although alternative fuels such as uranium nitride, uranium carbide, and metallic fuels have been investigated because of their higher thermal conductivity or higher uranium density, UO_2 remains the reference fuel for commercial light-water reactors. This is mainly due to its chemical stability, high melting temperature, irradiation tolerance, and extensive industrial experience [20]. Therefore, improving the understanding of UO_2 processing and structural behaviour remains relevant even as advanced fuel concepts continue to be developed [21].

2.2 Fabrication routes for UO_2 fuel pellets

Industrial fabrication of UO_2 fuel pellets generally involves powder preparation, pressing, and high-temperature sintering under a controlled atmosphere. Commercial UO_2 fuel pellets are typically fabricated to approximately 95–97% of the theoretical density (10.97 g/cm^{-3}) [22]. The aim is to produce dense ceramic pellets with controlled dimensions, sufficient mechanical integrity, and reproducible microstructure. Conventional sintering of UO_2 is typically carried out at high temperature, often around 1600–1700 °C, for several hours in reducing or controlled atmospheres [23, 24]. These processing conditions are used to promote densification and microstructural development suitable for fuel application.

The final quality of a sintered UO_2 pellet depends on both the starting powder and the applied processing conditions. Powder characteristics such as particle size, surface area, morphology, agglomeration state, and chemical homogeneity influence the achievable density and final microstructure [25]. Processing parameters such as temperature, heating rate, dwell time, atmosphere, and applied pressure further determine how the material consolidates during sintering. The general importance of particle bonding and neck formation during sintering has been reviewed by Mazlan et al. [26].

For UO_2 fuel fabrication, controlling the relationship between powder characteristics, sintering conditions, and final density is particularly important. High density is desirable because porosity reduces the effective thermal conductivity and can influence mechanical behaviour. However, the microstructure must also remain controlled, since excessive grain growth or non-uniform porosity can affect fuel performance [20]. Therefore, optimization of UO_2 processing requires an understanding of how fabrication parameters influence both densification and microstructure [27].

2.3 Spark plasma sintering

Spark plasma sintering (SPS) has been investigated as an alternative consolidation route for UO_2 [28]. Compared with conventional sintering, SPS can reduce processing time and sintering temperature by combining rapid heating with applied pressure. Because of these advantages, SPS has attracted interest as a laboratory-scale method for producing dense UO_2 and UO_2 -based materials [24, 29]. The technical principles of SPS are discussed in the Theory chapter.

Several studies have demonstrated the application of SPS to UO_2 . Ge et al. investigated the influence of temperature, holding time, and heating rate on the densification and properties of SPS-processed UO_2 pellets [29]. In a related study, they also examined the thermal conductivity of SPS-fabricated pellets and showed that density has a clear influence on thermal transport [24]. Other studies have extended SPS processing to commercial-size pellets, nanocrystalline UO_2 , and doped UO_2 -based systems [30, 31, 32, 33].

Recent work has also focused on understanding the parameters that control SPS densification of UO_2 . Balice et al. studied densification mechanisms in nearly stoichiometric UO_2 consolidated by SPS [34], while Margueret et al. investigated the effects of pressure, heating rate, and current during SPS of UO_2 nanopowders [35]. These studies show that SPS processing of UO_2 is sensitive to both powder properties and processing conditions.

Despite the increasing number of studies on SPS-fabricated UO_2 , systematic evaluation of processing parameters remains important. The same sintering conditions may lead to different final densities depending on the starting powder properties. Therefore, studying the combined influence of temperature, pressure, dwell time, and powder characteristics is necessary for assessing the practical limits of SPS as a processing route for UO_2 -based fuel materials.

2.4 Fission products and structural changes in oxide fuel

During reactor operation, UO_2 fuel undergoes continuous chemical and structural modification. Fission produces a wide range of elements that accumulate inside the fuel matrix. Depending on their chemical behaviour, these fission products may remain dissolved in the UO_2 matrix, form secondary oxide phases, precipitate as metallic particles, contribute to gas bubble formation, or segregate to grain boundaries. The chemical state of fission products in oxide fuels has been reviewed by Kleykamp, who showed that fission product behaviour depends on chemical affinity, oxygen potential, burnup, and temperature [6].

The accumulation of fission products is important because it can influence the structure, thermophysical properties, and long-term behaviour of the fuel [5]. Even when present at relatively low concentrations, these elements can modify the local chemistry of the UO_2 matrix. This is relevant for understanding changes in lattice parameter, thermal conductivity, mechanical response, and phase stability during irradiation. Computational and experimental studies have shown that fission-product-related defects and dopants can influence thermal transport and mechanical properties in UO_2 [11, 36].

Lanthanides are an important group of fission products in oxide nuclear fuel [37]. Their behaviour is relevant because they can interact with the UO_2 matrix and contribute to structural and chemical changes during burnup. Previous studies on rare-earth-doped UO_2 systems have shown that lanthanide incorporation can be linked to measurable lattice parameter changes and changes in uranium oxidation state [38, 39, 40]. These studies provide a basis for using controlled lanthanide-

doped UO_2 materials as simplified model systems for investigating fission-product effects.

Structural characterization is essential for evaluating such systems. X-ray diffraction can identify the fluorite UO_2 phase and detect crystalline secondary phases, while refined lattice parameters can reveal subtle structural changes caused by dopant incorporation or changes in stoichiometry. However, these changes can be small, especially at low dopant concentrations. High-resolution diffraction is therefore valuable for detecting lattice parameter variations that may be difficult to resolve using conventional laboratory XRD. This has been demonstrated, for example, in high-resolution synchrotron studies of doped UO_2 systems [41].

2.5 Simulated nuclear fuels

Direct experimental investigation of irradiated nuclear fuel is challenging because of high radioactivity, radiotoxicity, complex microstructure, and strict handling requirements. Spent nuclear fuel contains a mixture of actinides, fission products, activation products, and irradiation-induced defects. This complexity makes it difficult to isolate the influence of individual chemical or processing variables. The radiotoxicity and long-term hazard of spent fuel have been discussed in previous studies [8, 9].

Simulated nuclear fuels, or simfuels, provide a controlled approach for studying selected aspects of irradiated fuel behaviour. In simfuel materials, selected fission product elements are introduced into the UO_2 matrix under laboratory conditions. This allows specific chemical and structural effects to be investigated without the full radiological and microstructural complexity of real spent fuel. Simfuel materials can reproduce important chemical and microstructural features of high-burnup UO_2 -based fuel, including fission-product incorporation and second-phase formation [10].

Lanthanide-doped UO_2 represents a simplified simfuel system focused on selected fission-product effects. Controlled lanthanide doping allows the structural response of the UO_2 matrix to be studied in a much easier way than in irradiated fuel [37]. This approach is useful because the dopant type and concentration can be defined during synthesis, allowing the effect of selected elements to be investigated systematically. Although real spent fuel contains a more complex mixture of fission products, simplified doped systems are valuable for separating individual chemical contributions.

The production route is important in simfuel preparation because chemical homogeneity must be achieved before sintering. Wet-chemical methods, such as co-precipitation, can improve mixing between uranium and dopant species at the precursor stage. Co-precipitation has been used for mixed oxide systems and can produce powders suitable for subsequent calcination, reduction, and sintering [42]. For lanthanide-doped UO_2 , such an approach can help introduce the dopant before pellet fabrication and support more homogeneous incorporation into the final material [43, 44].

Despite their usefulness, simfuels remain an approximation of irradiated nuclear fuel and cannot reproduce all features developed during reactor operation [10]. In particular, it does not fully represent irradiation-induced microstructural changes,

such as defect accumulation, restructuring, burnup gradients, or fission-gas behaviour [45, 46, 47]. Its chemical composition is also simplified, since only selected fission-product surrogates are introduced, while real spent fuel contains a much broader range of fission products and actinides with different oxidation states and chemical interactions. Consequently, simfuels are well suited for controlled studies of selected compositional and structural effects, but it cannot completely reproduce the chemical, microstructural, and irradiation history of real spent nuclear fuel.

3

Theory

3.1 Crystal structure of UO_2

Uranium dioxide (UO_2) crystallizes in the fluorite structure (space group $Fm\bar{3}m$), in which uranium cations occupy the face-centered cubic lattice sites and oxygen anions are located in the tetrahedral interstitial positions. In its stoichiometric form, uranium is present as U(IV) and the lattice parameter is approximately 5.471 Å at room temperature [19]. A key feature of this structure is its high defect tolerance, which allows the accommodation of both point defects and substitutional species without major structural rearrangement.

Non-stoichiometry in UO_2 is primarily governed by variations in oxygen content. Under oxidizing conditions, additional oxygen atoms are incorporated into the lattice, leading to partial oxidation of uranium to higher valence states. This process is associated with the formation of defect clusters and changes in lattice parameter and transport properties [48]. These defect mechanisms are directly relevant for understanding both the thermodynamic behaviour of UO_2 and its response to processing conditions.

The structural flexibility of the fluorite lattice also enables the incorporation of foreign cations, including fission products. This characteristic is fundamental for the use of UO_2 as a model system in nuclear materials research, where controlled compositional modifications are used to probe defect chemistry and structural response [10]. In the present work, this property is exploited to investigate the incorporation of lanthanide dopants and their effect on the lattice. The fluorite crystal structure of UO_2 is illustrated schematically in Figure 3.1 .

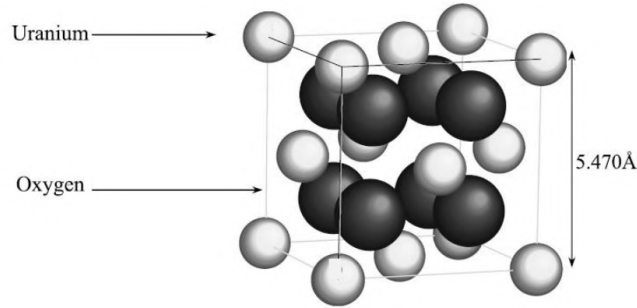


Figure 3.1: Schematic representation of the fluorite crystal structure of UO_2 . Source:[1].

3.2 Charge compensation in uranium oxide

Stoichiometric UO_2 contains uranium in the tetravalent oxidation state, U(IV). Under oxidizing conditions or following aliovalent substitution, a fraction of the uranium may be oxidized to U(V), resulting in non-stoichiometric UO_{2+x} while retaining the fluorite structure over a limited composition range. This redox flexibility plays a central role in charge compensation when aliovalent cations are incorporated into the fluorite lattice [18, 36].

When a trivalent ion substitutes for U(IV) on the cation sublattice, a local negative charge imbalance is introduced. One possible compensation mechanism is the partial oxidation of U(IV) to U(V), which restores electroneutrality through electronic rearrangement rather than through the formation of lattice vacancies. In this case, charge balance may be approximated by a simple stoichiometric relation between dopant concentration and the fraction of oxidized uranium [12, 49, 50].

Alternatively, compensation may occur through the formation of point defects in the oxygen sublattice, such as oxygen vacancies or interstitials, depending on thermodynamic conditions such as oxygen potential and temperature. The dominant mechanism is therefore governed by the defect chemistry of the system and the processing environment [51].

Because U(V) has a smaller effective ionic radius than U(IV), changes in uranium oxidation state are often reflected in measurable variations in lattice parameter. As a result, structural characterization techniques such as high-resolution diffraction can provide indirect insight into charge compensation behavior in doped UO_2 systems [12, 13, 52].

3.3 Lanthanide incorporation in UO_2

Lanthanides represent a major fraction of the fission product inventory in irradiated nuclear fuel and are typically present as trivalent cations in oxide form [12]. When incorporated into the UO_2 lattice, Ln(III) ions substitute for U(IV) on the cation sublattice, introducing a charge imbalance that must be compensated to maintain electroneutrality.

Charge compensation can occur through multiple mechanisms, including the partial oxidation of uranium from U(IV) to U(V) or the formation of defects in the oxygen sublattice [18]. The dominant mechanism depends on the oxygen potential, dopant concentration, and processing conditions. In dilute systems, such as those investigated in this work, lanthanides are typically incorporated as a solid solution within the fluorite lattice without the formation of secondary phases [10].

The substitution of lanthanide ions also leads to systematic changes in the lattice parameter due to differences in ionic radii. These variations can be described using geometrical models and provide a direct way to assess dopant incorporation [52]. In this work, high-resolution powder diffraction is used to quantify these lattice changes and to evaluate the extent of charge compensation through changes in uranium oxidation state.

3.4 Hard-sphere model

The hard-sphere model is a simple geometrical approach used to relate the lattice parameter of an ionic crystal to the sizes of the ions occupying the crystal structure. In this model, ions are treated as rigid spheres with fixed ionic radii, and the crystal geometry is described by the contact distances between neighbouring cations and anions. Although this approximation does not include electronic structure, covalency, local relaxation, or complex defect chemistry, it provides a useful first-order description of how changes in ionic radius can influence unit-cell dimensions [19, 38].

For a structure in which the relevant cation–anion contact distance controls the lattice parameter, the general relationship can be written as:

$$d_{c-a} = r_c + r_a, \quad (3.1)$$

where d_{c-a} is the cation–anion distance, r_c is the cation radius, and r_a is the anion radius. The lattice parameter can then be related to this distance through a structure-dependent geometrical factor:

$$a = K (r_c + r_a), \quad (3.2)$$

where a is the lattice parameter and K is a geometrical constant determined by the crystal structure.

For materials containing more than one type of cation on the same crystallographic sublattice, the average crystal structure observed by diffraction can be approximated using an average cation radius. This average radius is calculated from the fractional occupancy and ionic radius of each cation species:

$$\bar{r}_c = \sum_i X_i r_i, \quad (3.3)$$

where X_i is the fraction of cation species i on the cation sublattice and r_i is its corresponding ionic radius. The calculated lattice parameter is then expressed as:

$$a_{\text{calc}} = K (\bar{r}_c + r_a). \quad (3.4)$$

Substitution of a host cation by a dopant with a different ionic radius changes $\bar{r}_c$ and can therefore lead to lattice expansion or contraction. If a dopant fraction x replaces part of a host cation sublattice, a simple two-cation average radius can be written as:

$$\bar{r}_c = (1 - x)r_{\text{host}} + xr_{\text{dopant}}, \quad (3.5)$$

where r_{host} and r_{dopant} are the ionic radii of the host and dopant cations, respectively.

In aliovalently doped oxides, the dopant oxidation state must also be considered because charge compensation may be required to maintain electroneutrality. This can occur through changes in the oxidation state of the host cation, formation of oxygen vacancies or interstitials, or other defect mechanisms. In a general case where several cation species contribute to the same sublattice, the average cation radius can therefore be written as:

$$\bar{r}_c = X_1 r_1 + X_2 r_2 + X_3 r_3 + \cdots, \quad (3.6)$$

with the condition that the cation fractions sum to unity:

$$\sum_i X_i = 1. \quad (3.7)$$

The hard-sphere model can therefore be used to compare experimentally measured lattice parameters with values expected from a proposed substitution and charge-compensation mechanism. In this approach, the ionic radii are selected from Shannon's effective ionic radii for the appropriate oxidation state and eight-fold coordination, consistent with the fluorite structure of UO_2 [52].

However, the model should be regarded as an approximate structural description rather than a complete representation of the material. Its strength lies in relating lattice parameter changes to ionic size and crystallographic arguments, whereas its limitation is that it cannot independently identify a unique defect or charge-compensation mechanism.

3.5 Fundamentals of sintering and densification

Sintering is a thermally activated process in which a compacted powder evolves into a dense solid through atomic diffusion. The driving force for this transformation is the reduction of surface energy associated with the large surface area of the initial powder particles. During sintering, particles form necks, pores shrink, and the overall density increases [26].

The densification behaviour is strongly controlled by the characteristics of the starting powder. Parameters such as particle size, specific surface area, and agglomeration state determine both the thermodynamic driving force and the diffusion distances involved in the process [53]. Powders with high surface area typically exhibit enhanced densification kinetics, while powders with larger particle size or low surface area tend to show slower densification and may reach a limiting density under given processing conditions [54].

In conventional sintering, densification is achieved solely through thermally activated diffusion and therefore typically requires high temperatures and long dwell times [54]. The external heating of the sample can also generate temperature gradients between the surface and the interior, particularly for large samples, leading to non-uniform densification and microstructural development. Pressure-assisted sintering techniques, such as spark plasma sintering, have been developed to overcome some of these limitations by combining thermal activation with an applied mechanical load [55].

In addition to thermal activation, external pressure can significantly influence sintering behaviour. The application of pressure promotes particle rearrangement, increases the contact area between particles, and enhances neck formation through plastic deformation at interparticle contacts, particularly during the initial stages of densification [28, 34]. As sintering progresses, diffusion-controlled mechanisms become dominant. Understanding the transition between these regimes is essential for interpreting densification behaviour in pressure-assisted sintering techniques.

3.6 Spark plasma sintering

Spark plasma sintering (SPS) is a field-assisted sintering technique that combines uniaxial pressure with rapid resistive heating. In SPS, an electrical current is passed through a conductive die, typically made of graphite, generating Joule heating and enabling very high heating rates [56]. This allows the material to reach the target temperature within a short time, significantly reducing the total processing duration.

Compared with conventional sintering, SPS enables densification at lower effective temperatures and shorter dwell times, while limiting grain growth [56, 57]. The simultaneous application of pressure enhances particle rearrangement and accelerates densification, particularly during the early stages of sintering. As a result, SPS provides a powerful tool for studying densification mechanisms under controlled conditions. A schematic representation of the SPS setup is shown in Figure 3.2.

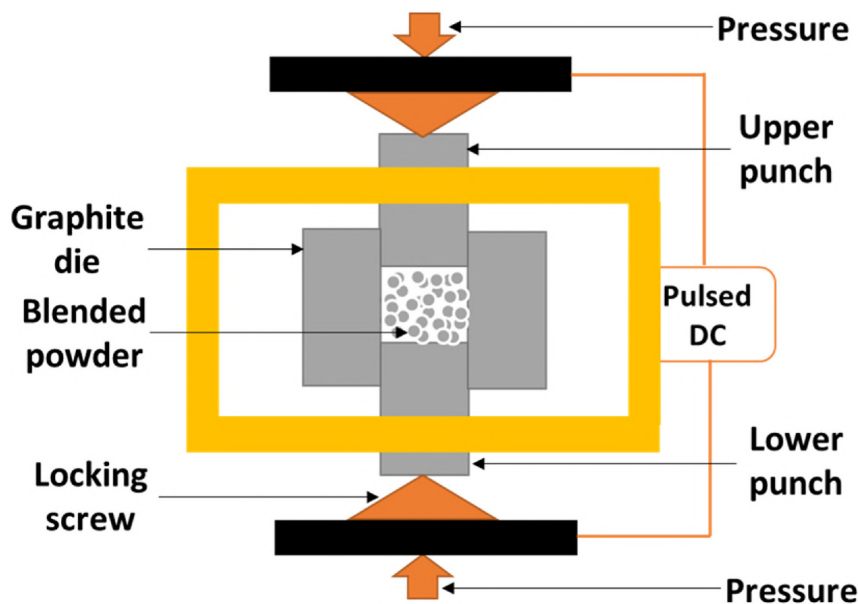


Figure 3.2: Schematic illustration of the spark plasma sintering (SPS) setup used for pellet fabrication. The powder compact is placed inside a graphite die between two graphite punches, while uniaxial pressure and pulsed direct current are simultaneously applied during sintering. Source:[2].

Although rapid Joule heating and applied pressure are generally considered the primary drivers of densification in SPS, the direct influence of the electrical current on mass transport remains a subject of ongoing discussion. Proposed current-assisted mechanisms include localized heating at particle contacts, enhanced grain-boundary diffusion, electromigration of charged defects, and the removal of surface contaminants or oxide layers. The relative contribution of these effects depends strongly on the electrical conductivity and microstructure of the material being processed and is still actively investigated [28, 58].

In the context of this work, SPS is used not only as a consolidation technique but also as a tool to investigate the relationship between processing parameters and densification behaviour. The independent control of temperature, pressure, and holding time enables the construction of a processing map, allowing the identification of dominant mechanisms and limiting factors. Particular attention is given to the role of the starting powder, as its characteristics are expected to strongly influence the achievable density.

4

Methods

4.1 Materials

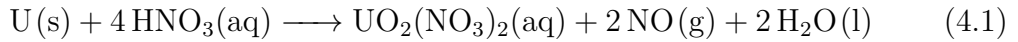
4.1.1 Pure UO_2 powder

The starting material for the SPS parameter mapping study was UO_2 powder supplied by Chalmers University. Prior to sintering, the powder was reduced in a tube furnace under a flowing atmosphere of 95 % Ar and 5 % H_2 at 1400 °C for 5 h in order to obtain a stoichiometry as close as possible to $\text{UO}_{2.00}$.

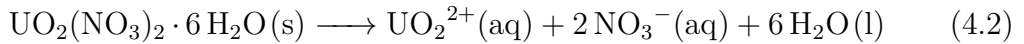
4.1.2 Lanthanide-doped UO_2 powders

Lanthanide-doped powders were synthesized by co-precipitation using metallic uranium and lanthanide nitrate precursors. Five compositions were prepared (La, Ce, Pr, Nd, and Gd), each with a nominal lanthanide concentration of 1 wt% of the total Ln + U mass.

Uranium metal was dissolved in 69 % nitric acid and later dried to form uranyl nitrate crystals:

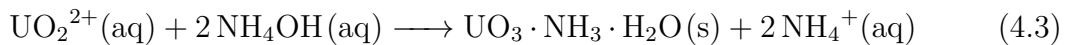


The resulting crystals were dissolved in MQ-grade water (18 M Ω cm) to obtain a 2.1 M uranyl nitrate solution:



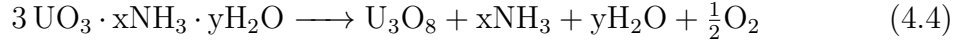
Lanthanide nitrate solutions were prepared in 0.1 M nitric acid using $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salts (La, Pr, Nd, Gd) and ceric ammonium nitrate for Ce. Each lanthanide solution was mixed with the uranyl nitrate solution to obtain a nominal lanthanide concentration of 1 wt% of the total Ln + U mass.

Co-precipitation was performed by adding the mixed solution dropwise into 28–30 % aqueous ammonia:

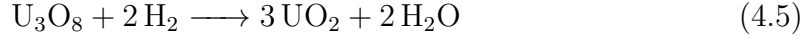


The precipitate was separated by centrifugation, washed twice with ultrapure water, and dried after ethanol dispersion.

Calcination was performed at 800 °C for 2 h in air:



Reduction to UO_2 was carried out at 1200 °C for 5 h under 5 % H_2/Ar :



A schematic overview of the synthesis and processing route for the lanthanide-doped UO_2 materials is shown in Figure 4.1.

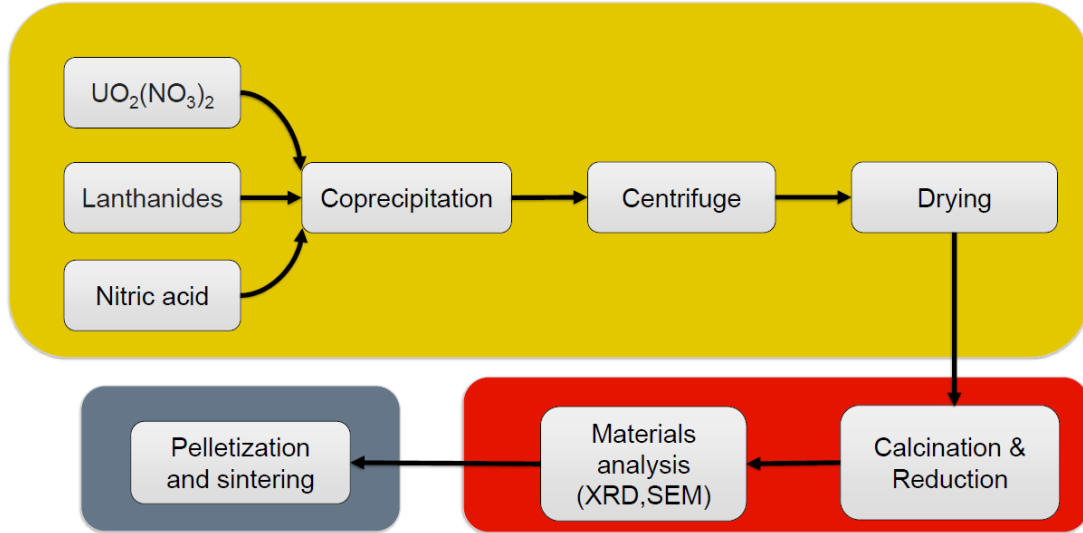


Figure 4.1: Schematic overview of the synthesis and processing route used for the lanthanide-doped UO_2 materials. Drawn by the author.

4.2 Powder characterization

Powder characterization was performed prior to SPS processing to determine the physical and structural properties of the starting materials. Specific surface area, morphology, and phase composition were evaluated using BET adsorption analysis, scanning electron microscopy, and X-ray diffraction, respectively.

4.2.1 BET surface area

The BET method estimates the specific surface area from nitrogen or krypton gas adsorption using the Brunauer–Emmett–Teller theory. The obtained surface area provides an indication of particle size and agglomeration state, which can influence sintering behaviour.

The specific surface area of both pure and doped powders was measured by krypton adsorption using a Micromeritics ASAP 2020 analyzer. Prior to measurement, powders were degassed at 300 °C under vacuum. Krypton adsorption–desorption isotherms were subsequently recorded at liquid nitrogen temperature, and the specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method.

4.2.2 Scanning electron microscopy (SEM)

Powder morphology and particle size were examined using a FEI Quanta SEM. Secondary electron images (SSD) were acquired at accelerating voltage of 15kV to evaluate particle morphology, particle size, and agglomeration behaviour. Micrographs were collected at multiple magnifications to provide information on the physical characteristics of the starting powders.

4.2.3 X-ray diffraction (XRD)

XRD analysis was used to verify the phase composition of the starting powder prior to SPS processing. The phase identification of the starting pure UO_2 powder was performed using a Bruker D8 Discover diffractometer operating in a locked-coupled θ - 2θ geometry. Diffraction patterns were collected over a 2θ range of 30 – 130° . The acquired data were analyzed using GSAS-II to assess phase purity and determine the lattice parameter of the fluorite UO_2 structure [59].

4.3 Spark plasma sintering

Spark Plasma Sintering (SPS) was performed at Stockholm University using a 530 ET SPS unit installed inside a glovebox. The temperature was monitored with a pyrometer aligned to the centre of the graphite die through a 1 mm aperture to ensure stable temperature acquisition above approximately 370°C . The graphite tooling and the SPS die during operation are shown in Figure 4.2 and Figure 4.3.

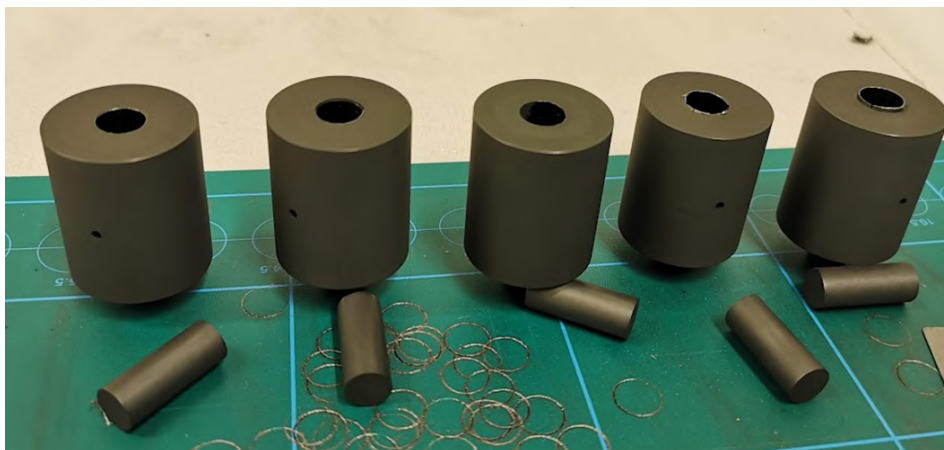


Figure 4.2: Graphite dies (8mm X 30mm) and punches used for SPS pellet fabrication. The dies have a small hole in the middle, where the pyrometer is aimed for more accurate temperature readings. Photo by the author.

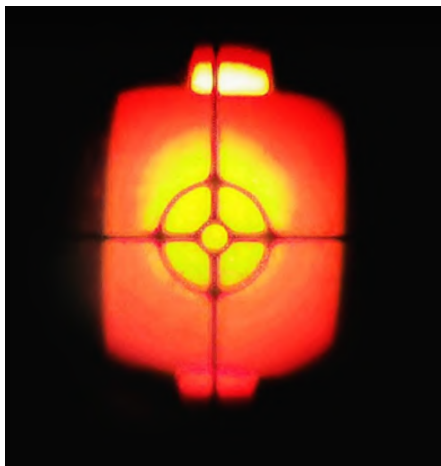


Figure 4.3: Graphite die during SPS heating, as seen through the optical scope of the pyrometer. Photo by the author.

4.3.1 Pure UO_2 powder sintering

For each pellet, 2 g of powder was loaded into a graphite die (8 mm diameter, 30 mm length). An initial preload of 26 MPa was applied. The temperature was increased to 400 °C within approximately 2 min, followed by heating at 100 °C min⁻¹ to the target temperature. Temperature was monitored using a pyrometer focused on the die centre. The whole sintering process was performed under vacuum. At 800 °C, the uniaxial pressure was increased manually to the target value at approximately 20 MPa min⁻¹. After the dwell time, samples were rapidly cooled under vacuum.

A total of 35 parameter combinations were investigated, with temperatures between 800 and 1500 °C, pressures between 60 and 160 MPa, and holding times between 1 and 15 min.

4.3.2 Lanthanide-doped UO_2 sintering

Five individual pellets were fabricated, corresponding to the La-, Ce-, Pr-, Nd-, and Gd-doped compositions. For each composition, 1 g of powder was loaded into an 8 mm graphite die. Sintering was performed at 1200 °C with a heating rate of 100 °C min⁻¹, under an applied pressure of 100 MPa and a dwell time of 15 min. The samples were cooled rapidly under vacuum after sintering and extracted using a hydraulic press.

4.4 Density determination

Density was determined using either the Archimedes method or helium pycnometry. The Archimedes method provides bulk density and is simple and suitable for comparing multiple pellets, but can be affected by open porosity, trapped gas, and wetting [60]. Helium pycnometry provides skeletal density with reduced sensitivity to surface effects, although closed porosity remains inaccessible to the gas. The two methods therefore measure slightly different density quantities.

4.4.1 Archimedes method (pure UO_2)

The density of the SPS-mapped pellets was determined using the Archimedes method. Each pellet was weighed in air and immersed in ethanol. Ethanol was selected as the immersion medium in order to minimize oxidation and improve wetting of the pellet surfaces. A stabilization time of at least 2 min was applied to allow trapped air to escape.

Two independent measurements were performed per pellet, and the reported density corresponds to the average value. The theoretical density of stoichiometric UO_2 (10.97 g cm^{-3}) was used to calculate the relative density [34].

4.4.2 Helium pycnometry (lanthanide-doped samples)

The density of the lanthanide-doped pellets was measured using helium pycnometry instead, which determines the true density by measuring the gas-accessible volume. The instrument used was a Micrometrics AccuPyc II 1340.

4.5 Microstructural analysis

Selected pellets from the pure UO_2 sintering study were analyzed to evaluate the effect of SPS parameters. Pellets 10, 18, and 24 were selected to study temperature effects at constant pressure, while pellet 34 was selected to study pressure effects. Additionally, two representative pellets from the lanthanide doping study were examined with the same method.

The samples were polished using silicon carbide papers followed by diamond suspensions down to $1 \text{ }\mu\text{m}$. SEM observations were performed in backscattered electron mode.

4.6 Chemical and structural characterization

The evaluation of dopant incorporation and densification behaviour in UO_2 -based materials requires a combination of structural, microstructural, and chemical characterization techniques. Diffraction methods are used to determine phase composition and lattice parameters, providing direct information on structural changes associated with dopant incorporation and defect formation. High-resolution powder diffraction is particularly sensitive to small variations in lattice parameter and enables the detection of minor secondary phases.

Microstructural characterization using scanning electron microscopy (SEM) provides insight into grain morphology, porosity, and densification state. These observations allow a direct correlation between processing conditions and the resulting microstructure, which is essential for interpreting densification behaviour.

Chemical analysis techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS provide information on dopant concentration and spatial distribution. In Figure 4.4 a series of pellets mounted in epoxy and polished is presented.



Figure 4.4: Lanthanide-doped UO_2 pellets mounted in epoxy prior to polishing and SEM microstructural analysis. Photo by the author.

4.6.1 ICP-MS

Lanthanide concentrations were determined by ICP-MS. ICP-MS provides high elemental sensitivity, with detection limits typically in the sub-ppb to ppb range, depending on the measurement conditions.

The powders were dissolved in 69 % nitric acid and diluted in 0.5 M nitric acid containing 1 ppb Bi as an internal standard. Measurements were performed using a Thermo Scientific iCAP Q instrument. One dissolved sample was analyzed for each composition, and ten replicate instrumental readings were performed for each sample. The resulting measurements were used to determine the lanthanide concentration of the synthesized powders.

4.6.2 High-resolution powder diffraction (HR-PXRD)

To evaluate subtle crystallographic changes induced by 1 wt% lanthanide substitution in the UO_2 matrix, high-resolution powder diffraction (HR-PXRD) measurements were performed at the Rossendorf Beamline (ROBL) of the European Synchrotron Radiation Facility (ESRF), Grenoble, France [61]. Because the dopant concentration is close to the detection limit of conventional laboratory XRD, synchrotron-based HR-PXRD was required to resolve small lattice parameter variations and to assess the potential presence of minor secondary phases.

Data were collected on the XRD-1 diffractometer in transmission geometry using an Eiger CdTe 500k detector (Dectris). The incident beam energy was calibrated using a Y metal foil and set to 17038 eV ($\lambda = 0.727692 \text{ \AA}$). The beam was focused to approximately $150 \times 150 \mu\text{m}^2$. Diffraction images were integrated using a dedicated Python routine based on PyFAI, adapted to treat series of images collected as a function of 2θ [62].

Approximately 10 mg of each lanthanide-doped UO_2 powder was mixed with borosilicate glass powder to a dilution of 30 mol%. This dilution was necessary to reduce X-ray self-absorption effects associated with uranium and to improve sample homogeneity. The powder mixtures were loaded into ultra-thin borosilicate capillaries (0.3 mm inner diameter, Hilgenberg). For safe handling of radioactive material, each capillary was placed inside a protective Kapton tube and sealed with epoxy resin. A brass pin was inserted at one end of the assembly to facilitate mounting on the HR-PXRD goniometer. A reference sample of pure UO_2 was measured under identical conditions for comparison.

The diffraction patterns were analysed by Rietveld refinement, in which a calculated diffraction pattern based on a crystallographic model is fitted to the measured data by least-squares optimization. Structural and instrumental parameters, including the lattice parameter, peak-profile terms, background, scale factor, and other relevant refinement variables, are adjusted iteratively to minimize the difference between the calculated and observed diffraction intensities. In this work, the Rietveld refinements were performed using GSAS-II [59], with particular emphasis on accurate determination of the fluorite UO_2 lattice parameter and identification of any additional crystalline phases.

The experimental mounting geometry and capillary used during the synchrotron HR-PXRD measurements at ROBL are presented in Figure 4.5 and Figure 4.6.

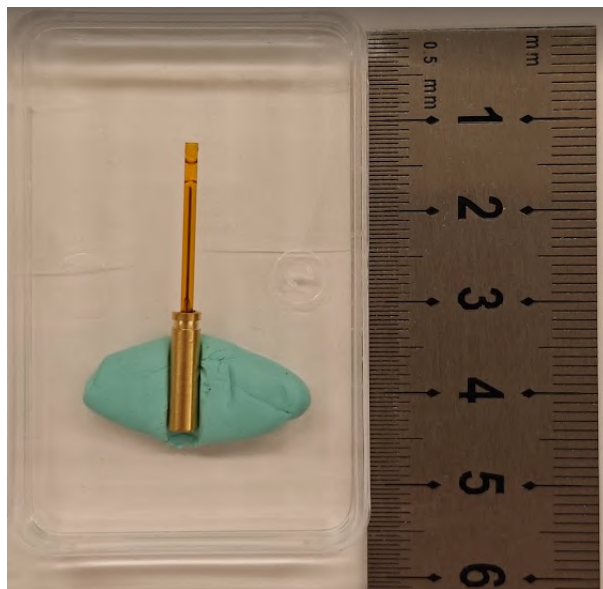


Figure 4.5: Thin glass capillary filled with the diluted powder. Each capillary was placed inside a protective Kapton tube and sealed with epoxy resin. A brass pin was inserted at one end of the assembly to facilitate mounting on the HR-PXRD goniometer. Photo by the author.



Figure 4.6: The XRD-1 diffractometer of the ROBL BM20 beamline (ESRF), showing the goniometer and capillary sample holder used for synchrotron measurements. Photo by the author.

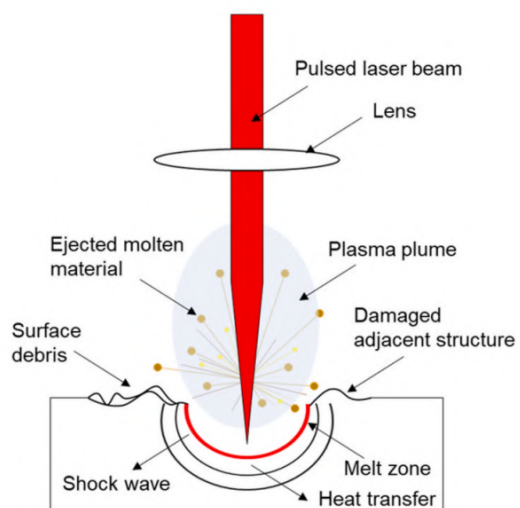
4.6.3 Laser ablation ICP-MS

Laser ablation ICP-MS measurements were performed at Studsvik Nuclear AB using a modified NWR 213 laser ablation system (Elemental Scientific Lasers LLC, Bozeman, MT, USA) designed for operation with radioactive samples in a shielded hot cell. The ablation chamber was connected to a PerkinElmer NexION 350D ICP-MS using a high-purity helium carrier gas, which transported the dry aerosol generated during laser ablation to the ICP-MS.

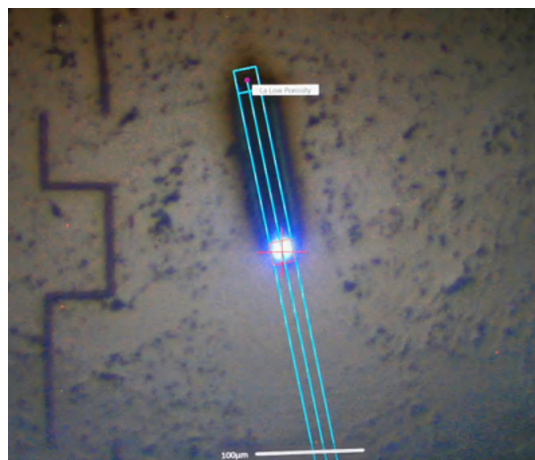
The ICP-MS employs a single quadrupole with a mass resolution of approximately 0.7 amu and therefore does not resolve monoatomic isobaric interferences, which are reported collectively. To protect the detector and improve sensitivity to trace components, the intense ^{238}U signal was attenuated by 99.98% using the instrument's quadrupole ion deflector.

A single 5000 μm line scan was performed on each pellet using a $20 \times 20 \mu\text{m}$ spot size, a scan speed of $25 \mu\text{m}, \text{s}^{-1}$, a pulse repetition rate of 20 Hz, and 25% laser power. During analysis, the pellet remained stationary behind a laser-transparent window while the motor-driven laser platform performed the scan [63]. The resulting signal profiles were used to evaluate the spatial stability of the lanthanide-to-uranium signal ratios across the pellet surfaces.

The principle of laser ablation and a representative line scan configuration used during the LA-ICP-MS measurements are illustrated in Figure 4.7.



(a) Schematic illustration of laser ablation during LA-ICP-MS analysis. Source:[64].



(b) A laser ablation line scan performed on a lanthanide-doped UO_2 pellet. Photo by the author.

Figure 4.7: Schematic and actual representations of the LA-ICP-MS measurements

5

Results

5.1 Pure UO_2 : SPS parameter mapping

5.1.1 Starting powder characterization

Phase composition and stoichiometry (XRD)

The crystallographic phase and oxygen stoichiometry of the starting UO_2 powder were evaluated by laboratory X-ray diffraction. The Rietveld refinement of the diffraction pattern is shown in Figure 5.1. The refinement confirms a single-phase fluorite structure without detectable secondary phases.

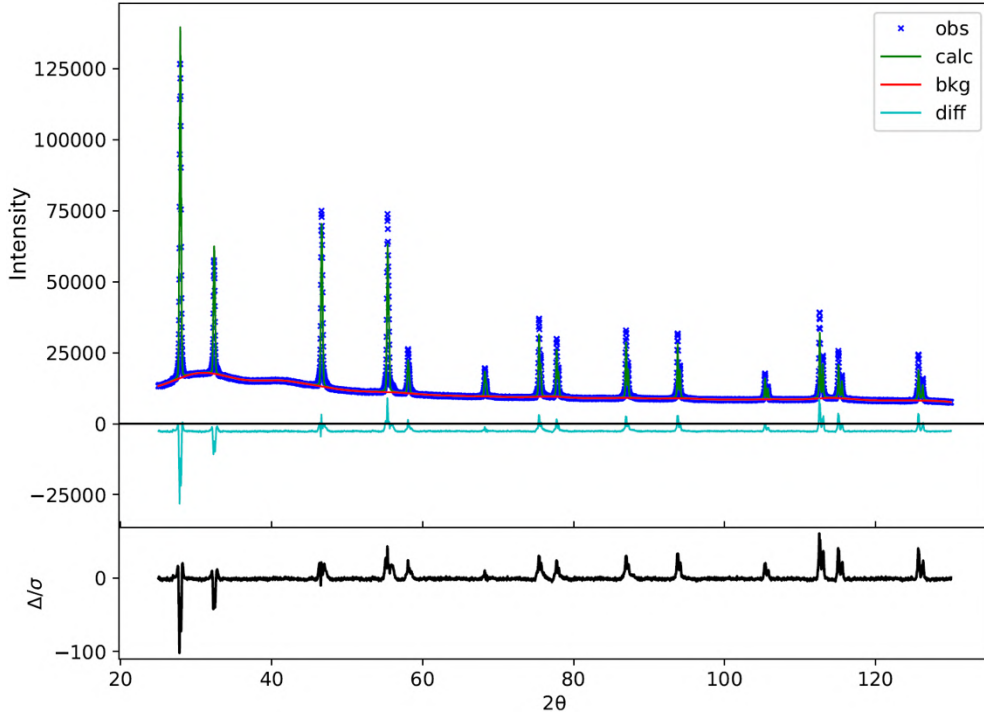


Figure 5.1: XRD refinement of the starting powder, showing a clear UO_2 phase.

The refined cubic lattice parameter was determined as

$$a_{\text{meas}} = 5.4709 \text{ \AA}.$$

To estimate the oxygen stoichiometry, the empirical Vegard-type relation valid for near-stoichiometric UO_2 ,

$$a(x) = a_0 - kx,$$

was applied, where $a_0 = 5.47127 \text{ \AA}$ is the lattice parameter of stoichiometric UO_2 at room temperature and $k = 0.13 \text{ \AA}$ per oxygen atom [19].

The lattice parameter difference,

$$\Delta a = a_0 - a_{\text{meas}} = 5.47127 - 5.47090 = 0.00037 \text{ \AA},$$

yields an oxygen deviation

$$x = \frac{\Delta a}{k} = \frac{0.00037}{0.13} = 2.85 \times 10^{-3}.$$

This corresponds to a nominal composition of

$$\text{UO}_{2+0.0029} \approx \text{UO}_{2.003}$$

Considering the typical uncertainty of laboratory Bragg–Brentano measurements (± 0.001 – $0.002 \text{ \AA}$), the associated uncertainty in oxygen content is approximately ± 0.01 . The material is therefore best described as

$$\text{UO}_{2.00 \pm 0.01}$$

Within the resolution of laboratory XRD, no statistically significant oxygen non-stoichiometry is detected. It should be noted that trace impurities in the starting UO_2 powder, if present, may influence the measured lattice parameter and thus introduce a small systematic uncertainty in the derived oxygen stoichiometry.

Specific surface area and morphology

The specific surface area of the starting powder was determined by krypton BET measurements, yielding

$$S_{\text{BET}} = 0.272 \pm 0.001 \text{ m}^2\text{g}^{-1}.$$

SEM observations reveal a homogeneous powder composed predominantly of small particles with limited agglomeration as presented in Figure 5.2. The particle morphology is consistent across different regions of the sample. Direct measurements from the SEM micrographs give a mean particle size of $1.8 \text{ }\mu\text{m}$, with a size distribution ranging from approximately 0.5 to $5 \text{ }\mu\text{m}$.

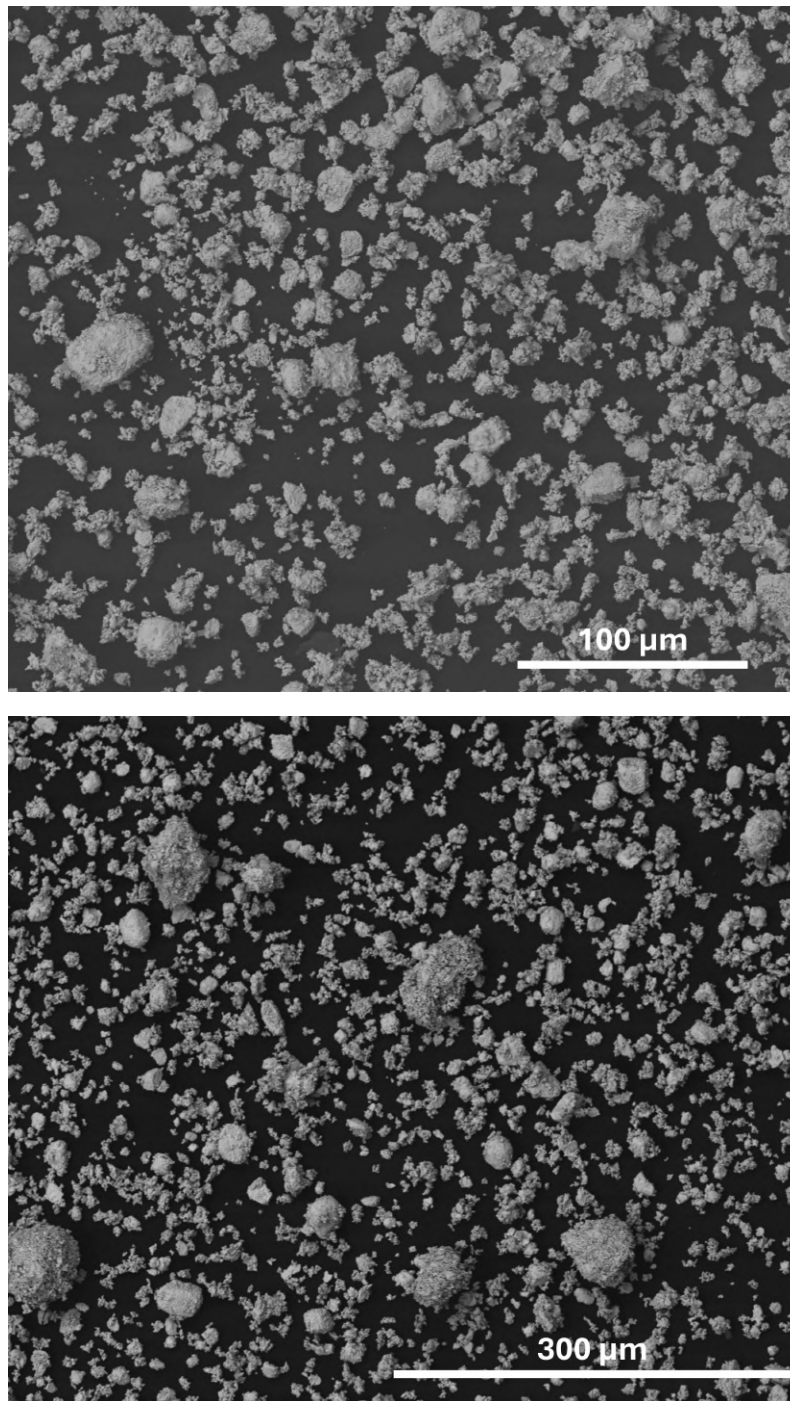


Figure 5.2: SEM micrographs of the starting UO_2 powder showing small particles with limited agglomeration.

The low specific surface area and the minor agglomeration indicate a relatively low surface energy driving force for sintering in subsequent SPS experiments.

5.1.2 Density measurement results

The bulk densities of the SPS-sintered UO_2 pellets were measured using the Archimedes method. Table 5.1 summarizes the investigated sintering conditions (800–1500 °C, 60–160 MPa, 1–15 min) and the corresponding relative densities, which ranged from 89.65% to 93.89% TD. The reported values are averages of two independent measurements per pellet, calculated using a theoretical density of 10.97 g/cm³ for stoichiometric UO_2 [34].

Table 5.1: Bulk density and relative density of SPS-sintered UO_2 pellets.

Pellet ID	P (MPa)	T (°C)	Time (min)	Density (g/cm ³)	TD (%)
1	120	1200	5	9.83 ± 0.08	89.65 ± 0.74
2	120	1400	5	10.18 ± 0.03	92.77 ± 0.27
3	120	1300	5	10.19 ± 0.03	92.92 ± 0.31
4	120	1350	5	10.23 ± 0.02	93.21 ± 0.21
5	120	1250	5	10.07 ± 0.08	91.81 ± 0.74
6	60	1400	5	10.10 ± 0.03	92.05 ± 0.25
7	60	1050	5	9.92 ± 0.09	90.41 ± 0.81
8	60	1250	5	9.91 ± 0.12	90.38 ± 1.13
9	60	1450	5	10.15 ± 0.01	92.52 ± 0.11
10	100	1200	5	9.99 ± 0.02	91.10 ± 0.15
11	60	1500	5	10.08 ± 0.02	91.86 ± 0.18
12	60	1200	5	10.02 ± 0.05	91.34 ± 0.41
13	60	1300	5	10.04 ± 0.05	91.53 ± 0.43
14	60	1350	5	9.96 ± 0.07	90.79 ± 0.65
15	100	1200	1	10.11 ± 0.07	92.18 ± 0.62
16	100	1200	15	10.04 ± 0.07	91.51 ± 0.68
17	100	1300	1	10.18 ± 0.02	92.75 ± 0.18
18	100	1300	5	10.17 ± 0.01	92.69 ± 0.08
19	100	1300	15	10.12 ± 0.05	92.24 ± 0.48
20	100	1400	1	10.23 ± 0.12	93.24 ± 1.09
21	100	1400	5	10.17 ± 0.03	92.69 ± 0.27
22	100	1400	15	10.16 ± 0.08	92.60 ± 0.73
23	100	1500	1	10.15 ± 0.18	92.54 ± 1.63
24	100	1500	5	10.17 ± 0.02	92.70 ± 0.15
25	100	1500	15	10.30 ± 0.01	93.89 ± 0.13
26	120	1500	5	10.23 ± 0.01	93.21 ± 0.10
27	130	1300	5	10.17 ± 0.02	92.67 ± 0.20
28	100	1300	5	10.11 ± 0.02	92.12 ± 0.16
29	100	1300	5	10.16 ± 0.07	92.57 ± 0.61
30	100	1400	1	10.17 ± 0.04	92.68 ± 0.33
31	100	1400	1	10.14 ± 0.04	92.40 ± 0.38
32	140	1300	5	10.21 ± 0.02	93.03 ± 0.17
33	150	1300	5	10.21 ± 0.02	93.03 ± 0.21
34	160	1300	5	10.20 ± 0.05	92.99 ± 0.44
35	60	800	5	10.04 ± 0.01	91.55 ± 0.05

5.1.3 Punch displacement during SPS

The axial punch displacement recorded during SPS provides real-time information on the densification behavior of the powder compact.

The displacements as a function of time for experiments conducted at a maximum temperature of 1300 °C with a holding time of 5 min, while varying the applied pressure between 60 and 160 MPa are presented in Figure 5.3. All experiments were performed using 2 g of powder per pellet to ensure comparable initial sample geometry.

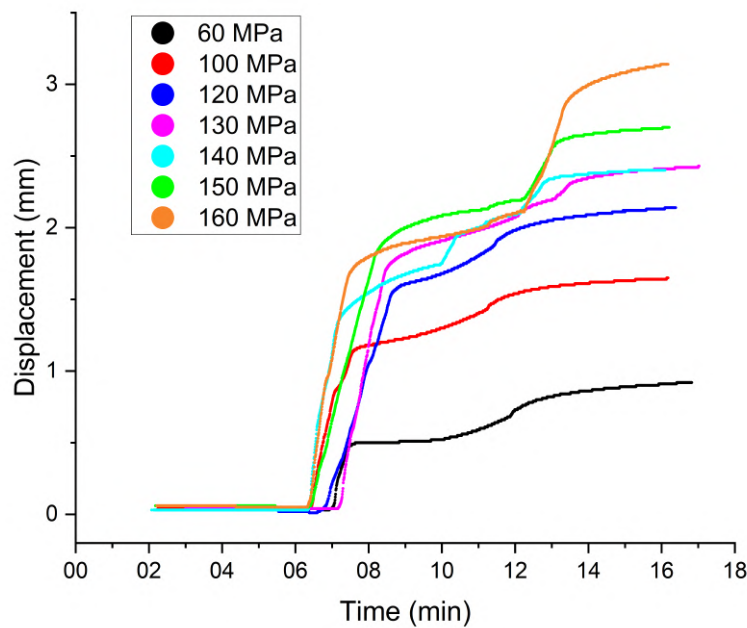


Figure 5.3: Axial punch displacement as a function of time during SPS at 1300 °C with a 5 min dwell, showing the influence of applied pressure. The recorded displacement includes contributions from both sample densification and the thermal and mechanical response of the graphite tooling and SPS assembly.

In all cases, the displacement remains nearly constant during the initial heating stage. A rapid increase in displacement occurs after approximately 800 °C, corresponding to the onset of the pressure ramp. This stage is followed by a slower approach toward a plateau during the dwell period.

Lower pressures (60 and 100 MPa) result in smaller total displacement, whereas higher pressures (120–160 MPa) produce significantly larger final displacement values. The increase in displacement with pressure is consistent with enhanced particle rearrangement and compaction under higher mechanical load, although the measured signal also contains contributions from the tooling response.

For the experiment performed at 160 MPa, an additional increase in displacement is observed during the later stages of the run. This behavior is attributed to minor deformation of the graphite tooling rather than further pellet densification.

The graphite die material (Mersen grade 2333) has a reported compressive strength of approximately 167 MPa. Since the applied pressure approaches this mechanical limit, small elastic or plastic deformation of the die cannot be excluded. Such deformation would artificially increase the recorded displacement without a proportional increase in pellet density.

Figure 5.4 presents displacement curves obtained at constant pressure of 100 MPa and holding time of 5 min, while varying the maximum temperature between 1200 °C and 1500 °C. The 5 min sintering time was selected as it is a frequently selected time for UO₂ spark plasma sintering [29, 55, 65].

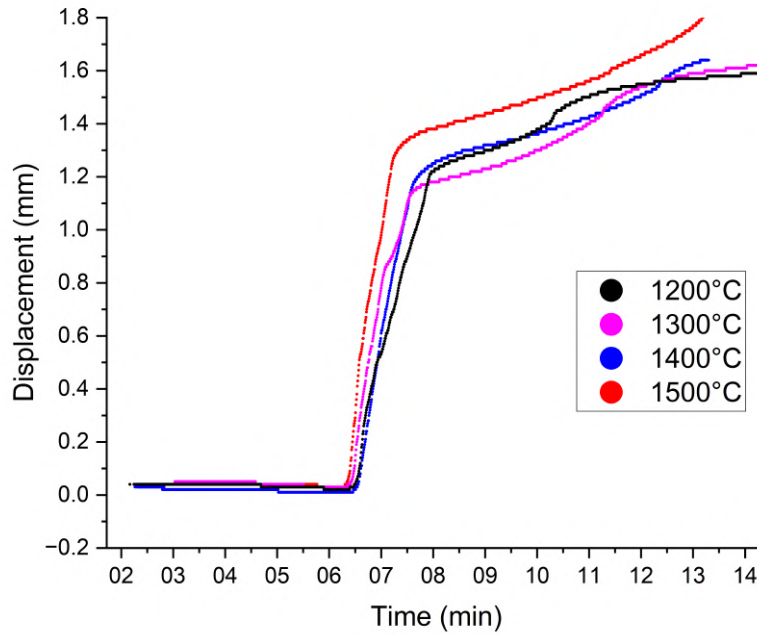


Figure 5.4: Axial punch displacement as a function of time during SPS at 100 MPa and 5 min holding time for four different maximum temperatures. The recorded displacement includes contributions from both sample densification and the thermal and mechanical response of the graphite tooling and SPS assembly. The two lowest temperatures, 1200 °C and 1300 °C lead to a displacement plateau. At 1400 °C and at 1500 °C the displacement shows a slight increase which is attributed to tooling deformation.

A similar displacement profile is observed for all temperatures. The displacement remains minimal during early heating and increases rapidly once the pressure ramp begins near 800 °C. Higher maximum temperatures lead to greater total displacement, indicating increased densification at elevated temperatures under constant mechanical loading.

5.1.4 Effect of sintering temperature on relative density

To evaluate the influence of temperature under fixed mechanical conditions, a series of pellets was sintered at a constant pressure of 100 MPa and a holding time of 5 min, while varying the maximum temperature between 1200 °C and 1500 °C. The resulting relative densities are shown in Figure 5.5.

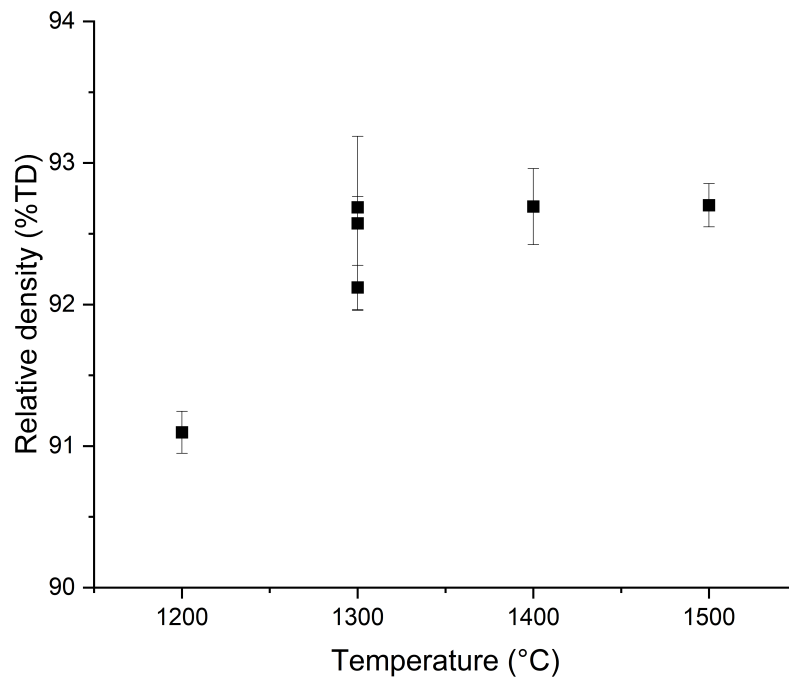


Figure 5.5: Relative density (%TD) as a function of temperature at 100 MPa and 5 min holding time, showing the increase of the relative density with applied temperature. The uncertainties are calculated based on the duplicate density measurements.

An overall increase in relative density with increasing temperature is observed. The relative density rises from approximately 91% at 1200 °C to about 92.7% at 1500 °C. The increase is most pronounced between 1200 and 1300 °C, while further temperature increases produce only moderate additional densification. This behavior indicates that temperature enhances densification, although a plateau tendency becomes apparent at higher temperatures within the investigated range.

5.1.5 Effect of applied pressure on relative density

To isolate the influence of applied pressure, pellets were sintered at a constant temperature of 1300 °C and a holding time of 5 min, while varying the uniaxial pressure from 60 to 160 MPa. The corresponding relative densities are presented in Figure 5.6.

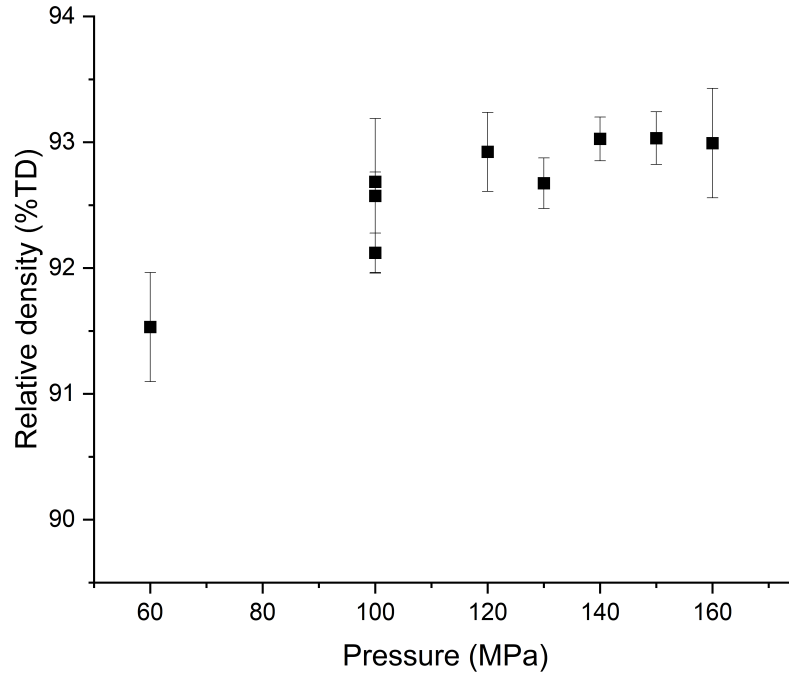


Figure 5.6: Relative density (%TD) as a function of pressure at 1300 °C and 5 min holding time showing the increase of the relative density with applied pressure.

The relative density increases with applied pressure. A clear improvement is observed when increasing the pressure from 60 MPa to 100 MPa. Beyond 120 MPa, the increase in density becomes smaller, and values approach approximately 93% TD. This trend indicates that pressure promotes particle rearrangement and compaction, although the densification gain becomes limited at higher pressures.

5.1.6 Pressure - temperature densification map

To provide an overview of the densification behavior, the relative density obtained for all pellets sintered with a holding time of 5 min was plotted as a function of both temperature and pressure. The resulting pressure–temperature map is shown in Figure 5.7.

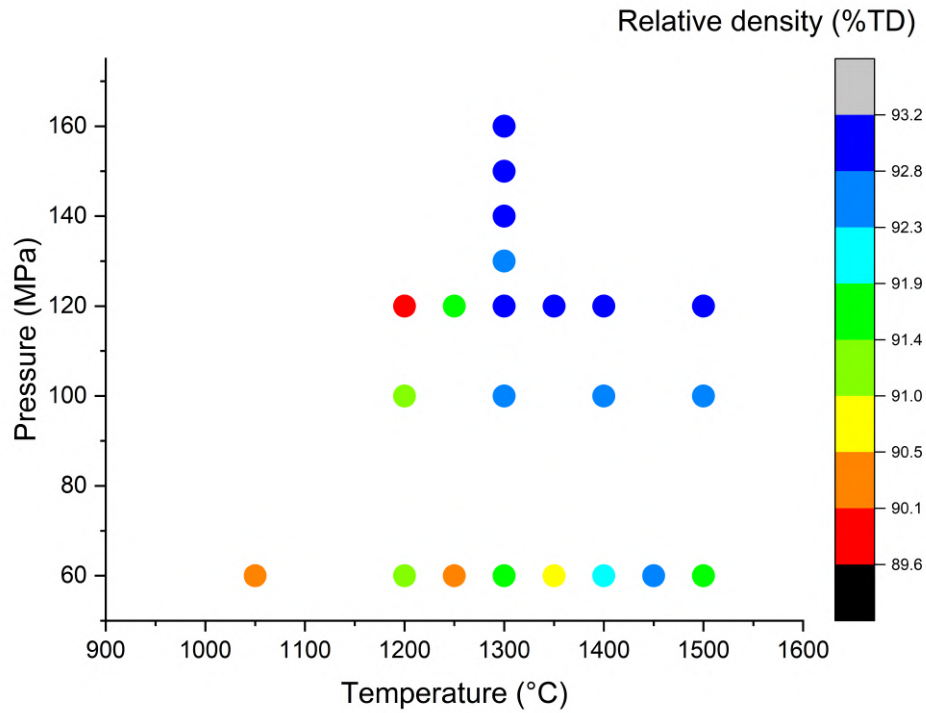


Figure 5.7: Pressure–temperature map of relative density (%TD) for a holding time of 5 min. The highest densities are indicated with blue colour on a limited region at elevated temperature and moderate high pressure.

The map illustrates a general increase in relative density with both temperature and pressure. However, the highest densities are confined to a limited region at elevated temperature and moderate to high pressure. The map also reveals a tendency toward densification saturation, as further increases in temperature or pressure do not lead to substantial improvements beyond approximately 93–94% TD.

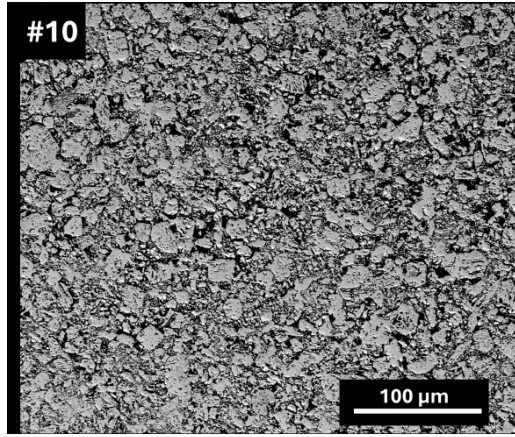
5.1.7 Quantitative porosity analysis by ImageJ

To complement the bulk density measurements, selected pellets representative of different regions of the SPS parameter space were analyzed by SEM and quantified using ImageJ software [66]. The measured two-dimensional pore fractions are summarized in Table 5.2.

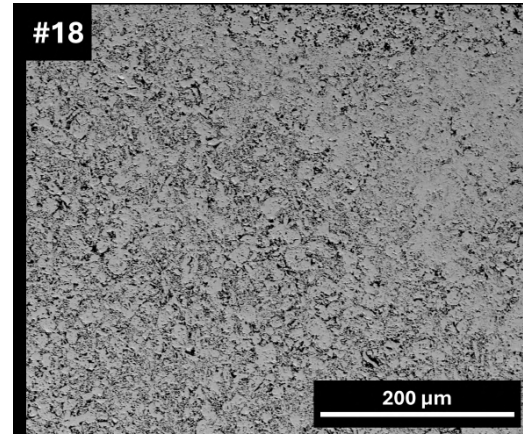
Table 5.2: Porosity determined by ImageJ analysis for selected UO_2 pellets.

Pellet ID	Sintering conditions	Surface porosity (%)
10	100 MPa – 1200°C – 5 min	21.8 ± 0.7
18	100 MPa – 1300°C – 5 min	5.6 ± 0.2
24	100 MPa – 1500°C – 5 min	4.8 ± 0.1
34	160 MPa – 1300°C – 5 min	4.4 ± 0.1

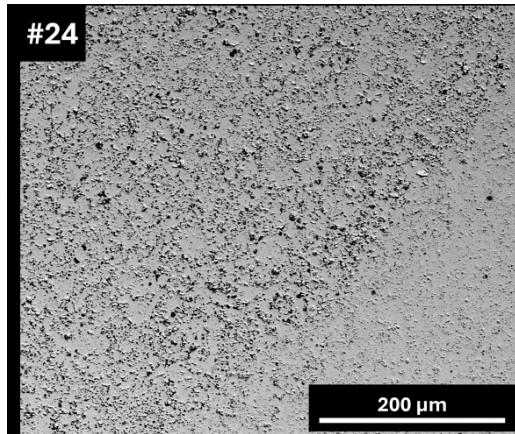
Representative SEM micrographs are shown in Figure 5.8. The images illustrate the reduction in pore fraction with increasing temperature and pressure. Pellet 10 exhibits significant residual porosity, whereas pellets 18, 24, and 34 show a more compact microstructure with fewer and smaller pores.



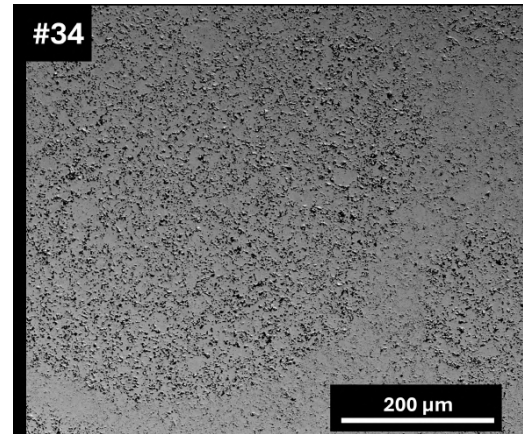
(a) Pellet 10 – 100 MPa – 1200°C – 5 min



(b) Pellet 18 – 100 MPa – 1300°C – 5 min



(c) Pellet 24 – 100 MPa – 1500°C – 5 min



(d) Pellet 34 – 160 MPa – 1300°C – 5 min

Figure 5.8: Backscattered SEM micrographs of selected pure UO_2 pellets sintered under different SPS conditions, illustrating the evolution of porosity and particle bonding with increasing temperature and pressure.

5.1.8 Correlation between punch displacement and relative density

To examine the relationship between axial shrinkage and final densification, the final punch displacement values were plotted against the measured relative densities for pellets sintered with a holding time of 5 min as shown in Figure 5.9). The dashed line is included solely as a guide to the eye.

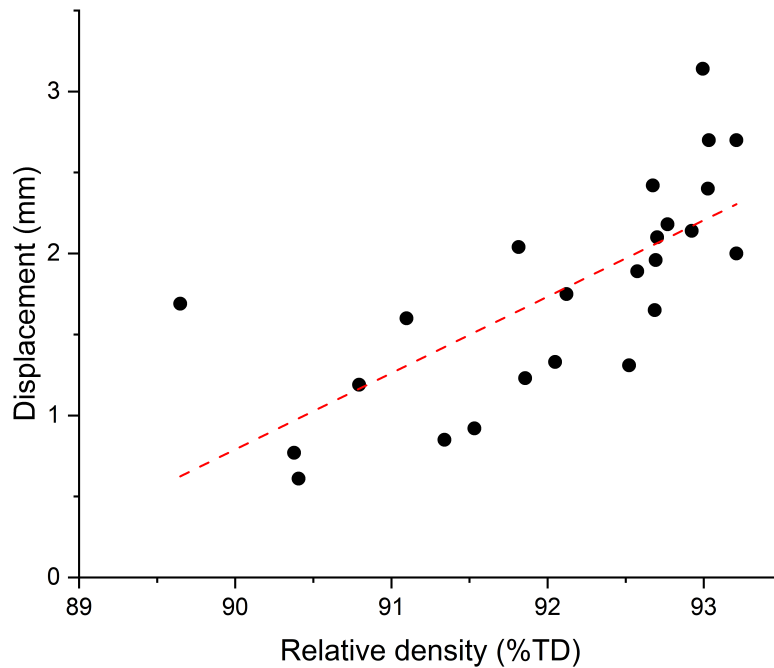


Figure 5.9: Final punch displacement as a function of relative density for pellets sintered with 5 min holding time, showing a correlation between displacement and relative density. Minor deviations at high displacement may reflect tooling deformation under elevated pressure. The dashed line is included solely as a guide to the eye.

A positive correlation between displacement and relative density is observed. Higher final displacement values generally correspond to higher relative densities, indicating that the recorded axial shrinkage reflects the overall densification process.

5.2 Lanthanide-doped UO₂

5.2.1 Powder ICP-MS analysis results

The chemical composition of the synthesized powders was verified by ICP-MS analysis. The measurements were performed on 100k-fold diluted solutions, and the measured elemental concentrations are summarized in Table 5.3 in nM.

The lanthanide mass fraction was calculated from the measured molar concentrations according to

$$w_{\text{Ln}} = \frac{c_{\text{Ln}}M_{\text{Ln}}}{c_{\text{Ln}}M_{\text{Ln}} + c_{\text{U}}M_{\text{U}}} \times 100, \quad (5.1)$$

where c denotes the measured molar concentration and M the corresponding molar mass. Since the lanthanide and uranium concentrations were determined from the same diluted solution, the common dilution factor cancels and does not affect the calculated composition. Calibration standards were used to account for differences in ICP-MS sensitivity between uranium and the individual lanthanides.

One dissolved sample was analyzed for each composition, with replicate instrumental readings used to evaluate measurement repeatability. The resulting uncertainties therefore represent instrumental repeatability rather than variability between independently prepared powder samples.

Table 5.3: ICP-MS results of the 100k-fold diluted dissolved powder samples, showing the measured lanthanide and uranium concentrations and the corresponding calculated lanthanide mass fractions. The reported uncertainties are derived from the instrument-reported RSD values and represent instrumental repeatability. The measured compositions are close to the nominal target of 1 wt% lanthanide.

Dopant	Ln (nM)	²³⁸ U (nM)	Ln (wt%)
La	2.76 ± 0.07	139.16 ± 2.66	1.15 ± 0.04
Ce	3.00 ± 0.04	159.12 ± 2.66	1.10 ± 0.02
Pr	2.90 ± 0.09	145.95 ± 2.73	1.16 ± 0.04
Nd	2.75 ± 0.07	157.46 ± 2.25	1.05 ± 0.03
Gd	3.13 ± 0.08	173.75 ± 2.21	1.18 ± 0.03

The measured lanthanide mass fractions range from 1.05 to 1.18 wt%, demonstrating that all five compositions were produced close to the nominal target of 1 wt% lanthanide.

5.2.2 Specific surface area of starting powders (BET)

The BET specific surface areas of the synthesized powders are listed in Table 5.4.

Table 5.4: BET specific surface area of the precursor powders, indicating similar morphology of all the powders except of the Nd-doped one.

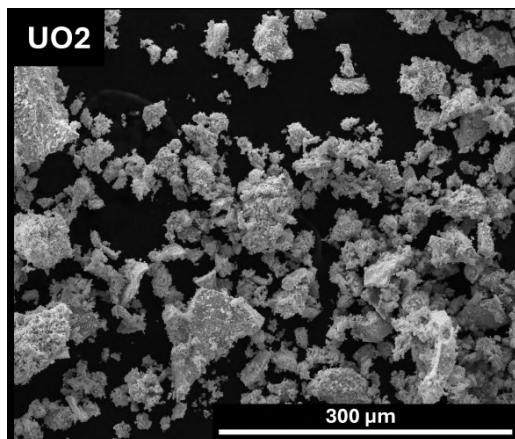
Sample	Surface area (m^2/g)
Pure UO_2	1.504 ± 0.004
1 wt% La- UO_2	1.463 ± 0.009
1 wt% Ce- UO_2	1.303 ± 0.003
1 wt% Pr- UO_2	1.541 ± 0.008
1 wt% Nd- UO_2	0.549 ± 0.001
1 wt% Gd- UO_2	1.594 ± 0.005

The pure UO_2 and the La-, Ce-, Pr-, and Gd-doped powders exhibit comparable specific surface areas, ranging from approximately 1.30 to 1.59 m^2/g . In contrast, the Nd-doped powder exhibits a substantially lower specific surface area of 0.55 m^2/g .

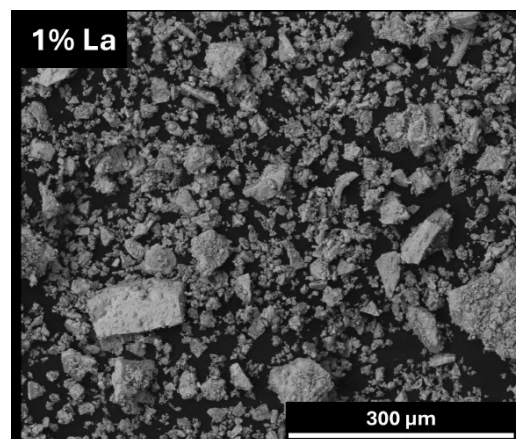
The pure UO_2 reference reported in Table 5.4 corresponds to the co-precipitated powder prepared as part of the lanthanide-doping study and is distinct from the low-surface-area UO_2 powder used for the SPS parameter-mapping experiments.

5.2.3 SEM analysis of starting powders

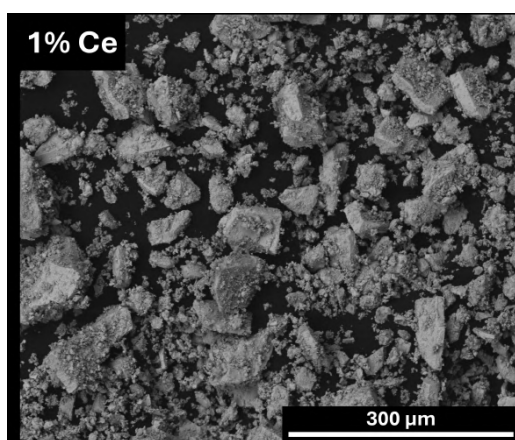
The morphology of the synthesized powders was examined by scanning electron microscopy prior to pellet fabrication. Representative micrographs of the pure and lanthanide-doped powders are shown in Figure 5.10.



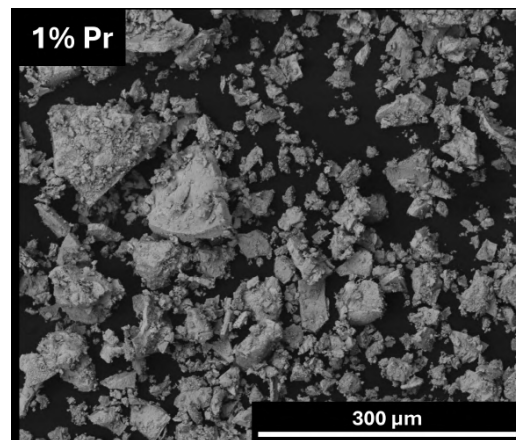
(a) Pure UO_2 powder.



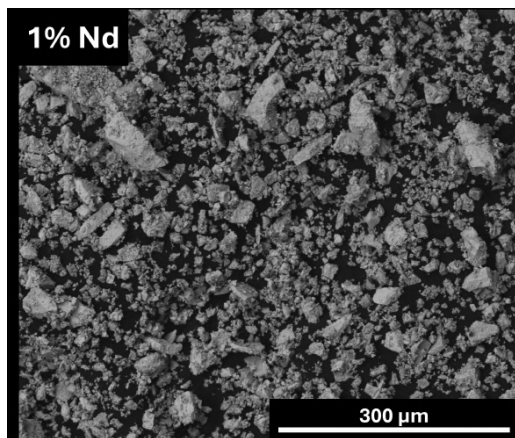
(b) 1 wt% La-doped UO_2 powder.



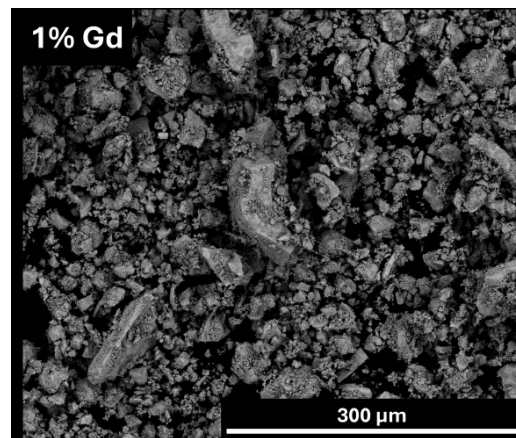
(c) 1 wt% Ce-doped UO_2 powder.



(d) 1 wt% Pr-doped UO_2 powder.



(e) 1 wt% Nd-doped UO_2 powder.



(f) 1 wt% Gd-doped UO_2 powder.

Figure 5.10: SEM images of pure and lanthanide-doped UO_2 precursor powders after reduction, showing irregular morphologies and similar agglomerated structures across the compositions.

All powders exhibit irregular particle morphologies with visible agglomeration at the micrometre scale. The general morphological characteristics are broadly comparable between the pure and lanthanide-doped powders, with no obvious systematic change in particle morphology associated with the different dopants at the resolution of the SEM measurements.

5.2.4 Pellet density measurements

The bulk densities of the five 1 wt% lanthanide-doped UO_2 pellets were measured using helium pycnometry. The measured densities, associated uncertainties, and calculated relative densities are presented in Table 5.5. The relative density was calculated using a theoretical density of 10.97 g/cm^3 for stoichiometric UO_2 [34]. As the dopant concentration is only 1 wt%, the theoretical density of pure UO_2 was used as a common reference value for all compositions to provide a consistent comparison of their densification behaviour.

Table 5.5: Helium pycnometry density results for the lanthanide-doped UO_2 pellets, showing measured densities and corresponding relative densities calculated using the theoretical density of pure UO_2 as a common reference.

Dopant	Density (g/cm^3)	Relative Density (%)
1 wt% Ce	10.682 ± 0.009	97.4 ± 0.1
1 wt% Nd	10.667 ± 0.042	97.2 ± 0.4
1 wt% La	10.763 ± 0.017	98.1 ± 0.2
1 wt% Pr	10.591 ± 0.034	96.5 ± 0.3
1 wt% Gd	10.627 ± 0.004	96.9 ± 0.1

All doped pellets exhibit high densification, with relative densities between 96.5% and 98.1% TD. The differences between dopants are small and remain within a narrow range, indicating comparable densification behavior under the applied SPS conditions.

5.2.5 Pellet microstructure (SEM analysis)

Microstructural characterization was performed on two representative pellets, namely the 1 wt% La- and 1 wt% Pr-doped UO_2 samples. High-magnification SEM micrographs of the polished pellet surfaces are shown in Figure 5.11.

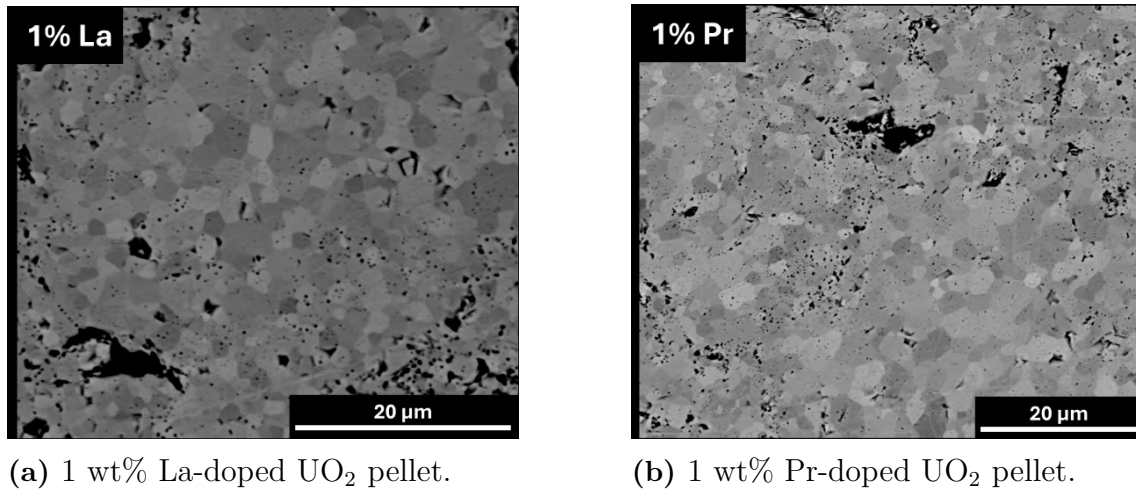


Figure 5.11: SEM micrographs of representative lanthanide-doped UO₂ pellets, showing limited porosity and small grain size.

Both samples exhibit dense microstructures with well-defined grains and limited residual porosity. The quantitative grain size analysis and measured porosity values are summarized in Table 5.6.

Table 5.6: Microstructural properties of 1 wt% La- and 1 wt% Pr-doped UO₂ pellets.

	1 wt% La	1 wt% Pr
Average grain size (μm)	2.03 ± 0.06	2.53 ± 0.87
Grain size range (μm)	0.9–3.7	0.9–5.1
Porosity (%)	6.33 ± 0.19	4.12 ± 0.12

The La-doped pellet exhibits an average grain size of 2.03 μm, while the Pr-doped sample shows a slightly larger average grain size of 2.53 μm. The overall grain size ranges from 0.9 to 3.7 μm for La and from 0.9 to 5.1 μm for Pr.

The measured porosity values are consistent with the high relative densities determined by helium pycnometry. The observed microstructures are characteristic of rapidly densified UO₂ processed by SPS [65].

5.2.6 High-resolution powder diffraction and lattice parameter modelling

High-resolution powder diffraction was used to assess the phase constitution of the pure and lanthanide-doped UO_2 samples and to determine their lattice parameters. Rietveld refinement of the HR-PXRD data confirmed that all samples crystallize in the fluorite UO_2 structure. Within the detection limits of the measurements, no secondary crystalline phases were observed. The refined lattice parameters obtained using GSAS-II are summarized in Table 5.7 [59].

Table 5.7: Refined lattice parameters obtained from HR-PXRD analysis using GSAS-II.

Composition	a_{meas} (Å)
Pure UO_2	5.47120(6)
1 wt% La	5.47198(3)
1 wt% Ce	5.46970(3)
1 wt% Pr	5.46969(3)
1 wt% Nd	5.46983(3)
1 wt% Gd	5.46790(3)

The lattice parameter refined for the pure UO_2 sample was 5.47120 Å, which is very close to the reported value of 5.47127 Å for stoichiometric UO_2 [19]. This agreement indicates that the reference UO_2 material used in this study was close to stoichiometric within the uncertainty of the diffraction measurement.

To examine whether the observed lattice parameter changes are consistent with substitutional incorporation of the lanthanide dopants, a simple geometrical hard-sphere model for the fluorite structure was applied [38]. The purpose of this model is not to fully describe the defect chemistry of doped UO_2 , but to provide a first-order comparison between the measured lattice parameters and the values expected from the ionic radii of the cations occupying the fluorite cation sublattice.

In the fluorite structure, the lattice parameter can be estimated from the average cation radius and the oxygen anion radius according to:

$$a_{\text{calc}} = \frac{4}{\sqrt{3}} (\bar{r}_c + r_{\text{O}^{2-}}), \quad (5.2)$$

where a_{calc} is the calculated lattice parameter, $\bar{r}_c$ is the average cation radius, and $r_{\text{O}^{2-}}$ is the ionic radius of oxygen. The average cation radius was calculated from the fractional occupancies of the cation sublattice:

$$\bar{r}_c = (X_{\text{U}^{4+}})(r_{\text{U}^{4+}}) + (X_{\text{U}^{5+}})(r_{\text{U}^{5+}}) + (X_{\text{Ln}})(r_{\text{Ln}}), \quad (5.3)$$

where X_i and r_i are the cation fraction and ionic radius of species i , respectively.

The lanthanide cation fraction, x , was calculated from the ICP–MS mass concentrations after conversion to molar fractions:

$$x = \frac{m_{\text{Ln}}/M_{\text{Ln}}}{m_{\text{Ln}}/M_{\text{Ln}} + m_{\text{U}}/M_{\text{U}}}, \quad (5.4)$$

where m_{Ln} and m_{U} are the ICP–MS measured mass concentrations of the lanthanide and uranium, respectively, and M_{Ln} and M_{U} are their corresponding molar masses.

For La, Pr, Nd, and Gd, the dopants were treated as trivalent cations substituting on the uranium sublattice. Charge compensation was represented by oxidation of an equivalent fraction of U(IV) to U(V). The corresponding cation fractions were therefore defined as:

$$X_{\text{Ln}^{3+}} = x, \quad X_{\text{U}^{5+}} = x, \quad X_{\text{U}^{4+}} = 1 - 2x. \quad (5.5)$$

Substitution into Eq. 5.2 gives:

$$a_{\text{calc}} = \frac{4}{\sqrt{3}} [r_{\text{O}^{2-}} + (1 - 2x)r_{\text{U}^{4+}} + xr_{\text{U}^{5+}} + xr_{\text{Ln}^{3+}}]. \quad (5.6)$$

For the Ce-doped sample, cerium was treated as tetravalent Ce(IV). This choice is supported by the use of ceric ammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, as the Ce precursor and by the experimentally observed lattice contraction relative to pure UO_2 . Since Ce(IV) is isovalent with U(IV), no additional U(V) charge compensation was included in this case. The cation fractions were therefore:

$$X_{\text{Ce}^{4+}} = x, \quad X_{\text{U}^{4+}} = 1 - x, \quad (5.7)$$

and the calculated lattice parameter was obtained from:

$$a_{\text{calc}} = \frac{4}{\sqrt{3}} [r_{\text{O}^{2-}} + (1 - x)r_{\text{U}^{4+}} + xr_{\text{Ce}^{4+}}]. \quad (5.8)$$

The ionic radii used in the calculations are listed in Table 5.8. The cation radii correspond to eightfold coordination, appropriate for the fluorite cation site [38, 52]. The oxygen ionic radius was taken as 1.368 Å, calculated from the fluorite geometry of stoichiometric UO_2 using $a_{\text{UO}_2} = 5.47127$ Å and $r_{\text{U}^{4+}} = 1.001$ Å.

Table 5.8: Ionic radii used in the geometrical ionic-radius model. Cation radii are given for CN = 8.

Ion	Ionic Radius (Å)
O^{2-}	1.368
U^{4+}	1.001
U^{5+}	0.880
La^{3+}	1.160
Ce^{4+}	0.970
Pr^{3+}	1.126
Nd^{3+}	1.109
Gd^{3+}	1.053

The calculated lattice parameters are compared with the experimentally refined HR-PXRD values in Table 5.9.

Table 5.9: Comparison between calculated and measured lattice parameters for pure and lanthanide-doped UO_2 .

Composition	x (Ln fraction)	a_{calc} (Å)	a_{meas} (Å)	$a_{\text{meas}}/a_{\text{calc}}$
Pure UO_2	0.0000	5.47097	5.47120	1.00004
1 wt% La	0.0195	5.47268	5.47198	0.99987
1 wt% Ce	0.0185	5.46965	5.46970	1.00001
1 wt% Pr	0.0195	5.47115	5.46969	0.99973
1 wt% Nd	0.0171	5.47046	5.46983	0.99989
1 wt% Gd	0.0177	5.46815	5.46790	0.99995

Overall, the calculated lattice parameters reproduce the main experimental trend observed by HR-PXRD. The La-doped sample shows a small lattice expansion relative to pure UO_2 , whereas the Ce-, Pr-, Nd-, and Gd-doped samples show lattice contraction. This behaviour is consistent with the combined effect of dopant ionic radius and charge compensation. In the trivalent lanthanide-doped samples, substitution by larger Ln(III) ions is partly counteracted by the formation of smaller U(V) ions. For La, the large ionic radius of La(III) is sufficient to produce a net lattice expansion, while for Pr, Nd, and especially Gd, the combined radius effect leads to contraction. The close values of $a_{\text{meas}}/a_{\text{calc}}$ to unity indicate that the simplified hard-sphere model captures the dominant size-related contribution to the lattice parameter variation, although it should be regarded as an approximate geometrical description rather than a complete defect chemical model.

Phase purity

Representative HR-PXRD refinements are shown in Figure 5.12. In all cases, the diffraction patterns are fully consistent with the fluorite UO_2 structure. No additional reflections attributable to secondary oxide phases or lanthanide-rich compounds are detected.

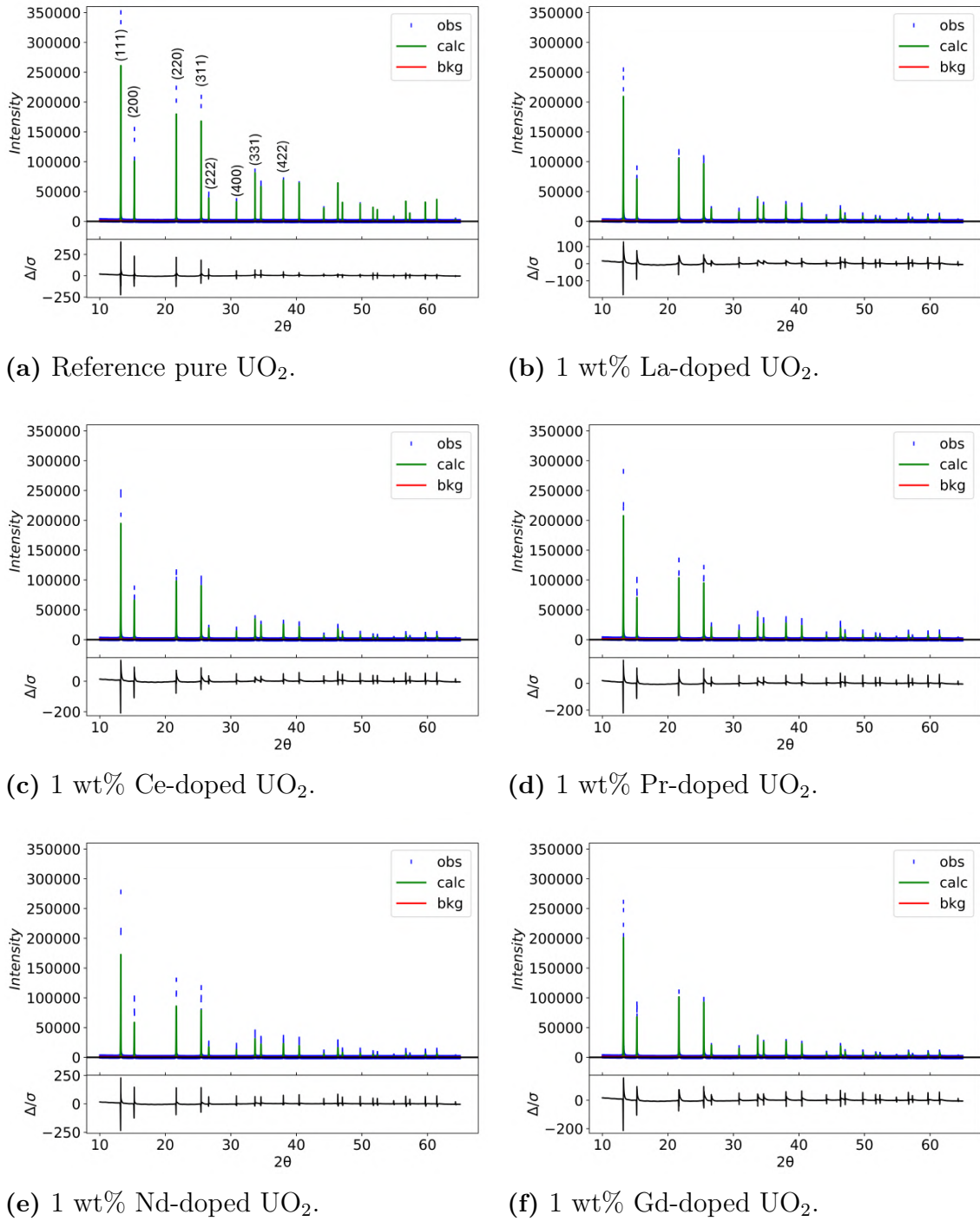


Figure 5.12: Rietveld refinements of HR-PXRD patterns for pure and lanthanide-doped UO_2 samples, confirming single-phase fluorite structures without detectable secondary phases. The principal crystallographic planes are indexed in the pure UO_2 pattern to indicate the characteristic reflections of the fluorite structure. In the legend, obs represents the observed diffraction data, calc the calculated Rietveld profile, and bkg the fitted background. The lower panel shows the normalized difference between the observed and calculated intensities, expressed as Δ/σ .

5.2.7 Laser ablation ICP-MS results

Laser ablation ICP-MS measurements were performed to evaluate the lanthanide signal response relative to the uranium matrix in the sintered UO_2 pellets. The lanthanide-to-uranium signal ratios ($\text{Ln}/^{235}\text{U}$) were calculated from the measured ion intensities of the selected lanthanide isotopes and ^{235}U .

The distribution of the measured $\text{Ln}/^{235}\text{U}$ signal ratios for the five lanthanide-doped samples (La, Ce, Pr, Nd, and Gd) is shown in Figure 5.13. Each box plot represents the statistical distribution of signal ratios recorded along the ablation tracks. The boxes correspond to the interquartile range, the central line indicates the median value, and the whiskers represent the overall spread of the measurements.

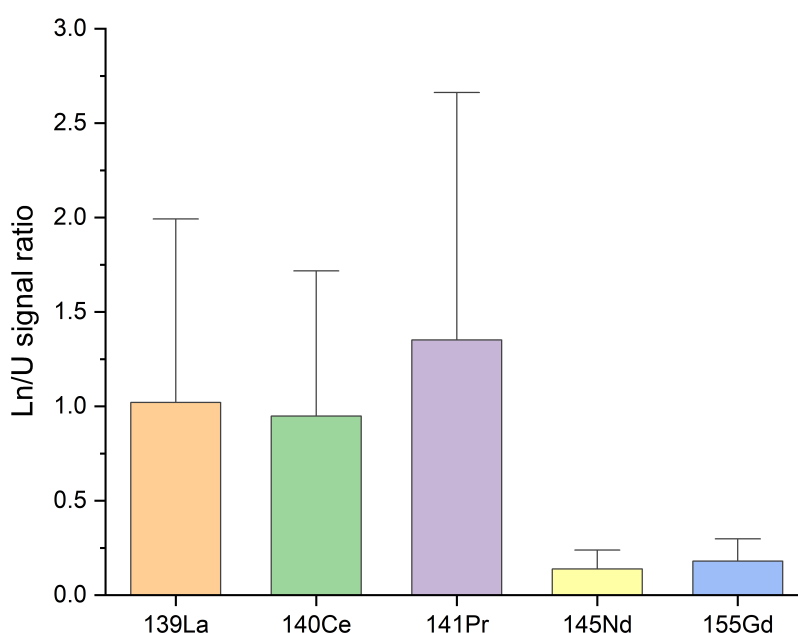


Figure 5.13: Box-plot distributions of $\text{Ln}/^{235}\text{U}$ signal ratios obtained during LA-ICP-MS measurements. Each box represents the interquartile range, the central line indicates the median, and the whiskers show the overall spread of the measured signal ratios along the ablation path. Differences in absolute signal levels between the lanthanides reflect, in part, differences in the natural isotopic abundances of the monitored isotopes and elemental ICP-MS response.

6

Discussion

The two experimental parts of this thesis address complementary aspects of UO_2 -based materials processed by spark plasma sintering. The first part establishes the densification behaviour of pure UO_2 over a broad pressure–temperature space. The second part applies SPS to chemically controlled lanthanide-doped UO_2 synthesized by wet co-precipitation and examined by advanced structural and chemical techniques. Together, the studies define a processing to structure framework: the pure UO_2 mapping identifies densification limits associated with a given starting powder, while the doped systems demonstrate how controlled chemistry combined with SPS yields dense and structurally well-defined surrogate materials.

6.1 Pure UO_2 densification behaviour

The SPS parameter map of pure UO_2 produced relative densities between approximately 89% and 94% of the theoretical density, as shown in Table 5.1. Although SPS has frequently been reported to produce near-theoretical densities in UO_2 , these studies commonly employ powders with finer particle sizes, higher specific surface areas, or different synthesis routes than the commercial micrometric powder investigated here [55]. The lower maximum density obtained in the present work therefore demonstrates that the densification behaviour is strongly influenced by the characteristics of the starting powder.

The initial powder exhibits a low specific surface area ($0.27 \text{ m}^2\text{g}^{-1}$) and a mean particle size of approximately $1.8 \text{ }\mu\text{m}$. Such morphology provides a relatively small surface-energy driving force for sintering while increasing the diffusion distances required for pore elimination. Consequently, pressure-assisted particle rearrangement and neck formation dominate the early stages of SPS, whereas further densification becomes increasingly diffusion-limited as the relative density approaches 93–94% TD. Although the punch displacement continues to increase slightly during the dwell, this signal does not solely represent sample densification, as it also includes contributions from graphite tooling deformation and the limited compressibility of the remaining closed porosity. The observed density plateau is therefore interpreted as being primarily controlled by the intrinsic characteristics of the starting powder rather than by insufficient SPS temperature, pressure, or holding time.

XRD analysis confirmed that the starting powder is essentially stoichiometric, with a composition of approximately $\text{UO}_{2.00\pm0.01}$. At this level, oxygen non-stoichiometry is not expected to significantly influence the densification behaviour, indicating that powder morphology and surface reactivity are the dominant factors

controlling the sintering response.

The punch displacement curves further clarify the densification sequence. As shown in Figures 5.3 and 5.4, a rapid increase in displacement occurs when pressure is applied at approximately 800 °C, corresponding to particle rearrangement and pressure-assisted compaction. This stage is followed by a slower displacement regime as the temperature continues to increase. However, the measured punch displacement includes contributions from sample densification as well as the thermal and mechanical response of the graphite tooling and SPS assembly, and should therefore not be interpreted as a direct quantitative measure of densification.

Increasing the sintering temperature from 1200 to 1300 °C produces a noticeable increase in density, whereas further increases to 1400 and 1500 °C result in only limited additional densification, as shown in Figure 5.5. A similar trend is observed for pressure, where increasing the applied pressure beyond approximately 100–120 MPa leads to only marginal improvements in the final density, as shown in Figure 5.6. The overall pressure–temperature behaviour and the tendency toward densification saturation are summarized in Figure 5.7.

The SEM porosity analysis further supports this trend, with reduced pore fractions observed at higher temperatures and pressures, as summarized in Table 5.2 and Figure 5.8. The positive relationship between final punch displacement and relative density is shown in Figure 5.9; however, at higher displacement values, part of the additional punch movement may arise from thermal expansion and mechanical deformation of the graphite tooling rather than from further densification of the compact.

Variations in holding time, as shown in Table 5.1, between 1 and 15 min do not produce systematic increases in density, confirming that most densification occurs during heating and the initial application of pressure. Once closed porosity is established, the remaining pores become increasingly difficult to eliminate, and prolonged holding provides little additional benefit.

The SEM observations support this interpretation. Pellets sintered at lower temperatures exhibit pronounced interparticle porosity, whereas those processed at higher temperatures and pressures show improved particle bonding and reduced porosity. However, even under the most aggressive SPS conditions, the original powder morphology continues to influence the final microstructure, indicating that the microstructural evolution remains constrained by the characteristics of the starting powder.

Overall, these results demonstrate that the densification of pure UO_2 during SPS cannot be studied solely in terms of processing parameters. While increasing temperature and pressure promotes particle rearrangement and diffusion, the achievable density is strongly constrained by the properties of the starting powder. This is further evidenced by the continued increase in punch displacement after the density has largely stabilized, showing that higher processing severity primarily contributes to tooling deformation rather than substantial additional densification of the sample.

6.2 Structural response of doped UO_2

In contrast, the lanthanide-doped systems were synthesized via wet chemical coprecipitation, enabling precise control of dopant incorporation. ICP-MS measurements confirm lanthanide mass fractions close to the targeted 1 wt%, demonstrating good compositional control during the co-precipitation synthesis, as shown in Table 5.3.

The doped pellets reach relative densities between 96.5% and 98.1% TD, higher than in the pure powder mapping study. Helium pycnometry and SEM observations, presented in Figure 5.11, show well-consolidated grains with limited residual porosity. The improved densification likely reflects the higher specific surface area and greater surface reactivity of the chemically derived precursor powders compared with the coarse pure UO_2 powder.

The precursor powders generally exhibited similar specific surface areas, between approximately 1.3 and 1.6 m^2/g , with the exception of the Nd-doped powder, which showed a substantially lower value of approximately 0.55 m^2/g , as shown in Table 5.4. Since each composition was precipitated, calcined, and reduced as a separate batch, this difference is most likely associated with batch-to-batch variations during powder processing than with a specific intrinsic effect of Nd incorporation. Small differences in precipitation, drying, calcination, or reduction may influence the accessible surface area of the final powder [67, 68, 69].

The SEM observations, shown in Figure 5.10, show broadly similar irregular particle morphologies and micrometre-scale agglomeration across the pure and lanthanide-doped powders. No clearly distinct morphology can be associated with any individual lanthanide at the resolution of the SEM measurements, indicating that the overall powder morphology is primarily governed by the common precipitation and thermal-treatment route.

HR-PXRD analysis confirms that all doped samples retain the fluorite UO_2 structure without detectable secondary phases, as shown in Figure 5.12. The refined lattice parameter of the reference UO_2 matches literature values, indicating that the synthesis and reduction procedures produced material close to the expected stoichiometry [1].

The significance of the HR-PXRD results lies not only in confirming the fluorite structure, but also in demonstrating that the lanthanide additions modify the host lattice in a systematic and measurable way. At the 1 wt% doping level, the absence of additional diffraction peaks indicates that no crystalline lanthanide-rich secondary phase is detected, while the reproducible shifts in lattice parameter show that the dopants influence the average fluorite lattice itself. Together, these observations provide structural evidence that the lanthanides are incorporated into the UO_2 matrix rather than simply being present as physically mixed or segregated oxide phases.

Systematic lattice parameter variations are observed across the lanthanide series, as summarized in Table 5.7. The La-doped sample shows a slight expansion, consistent with the larger ionic radius of La(III). The Ce-doped sample shows contraction, consistent with treating Ce as Ce(IV) within the model. The Pr, Nd, and Gd doped samples exhibit progressively smaller lattice parameters, reflecting the

combined effects of ionic size and charge compensation.

The lattice parameters calculated using the hard-sphere model are in very good agreement with the experimentally refined HR-PXRD values, as shown in Table 5.9. This indicates that, although the model is simplified, it describes the main influence of cation size and charge compensation on the observed lattice parameter variations [38, 70]. For La, Pr, Nd, and Gd, the calculations assume substitution of trivalent lanthanide ions on the uranium sublattice, with charge compensation occurring through oxidation of an equivalent fraction of U(IV) to U(V). For Ce, the dopant is treated as Ce(IV), in agreement with the Ce(IV) precursor chemistry and the observed contraction of the lattice. Therefore, no U(V) charge compensation is included for the Ce-doped sample.

The agreement between calculated and measured lattice parameters is important because the changes caused by 1 wt% lanthanide substitution are very small. Such small shifts are difficult to evaluate reliably using conventional laboratory XRD. The use of synchrotron HR-PXRD at ESRF provides the precision needed to resolve these subtle dopant-dependent lattice variations and to compare them with the ionic-radius-based model. Overall, the comparison supports the incorporation of the lanthanides into the fluorite UO_2 lattice and shows that the lattice parameter evolution is mainly controlled by effective cation radii and charge-compensation effects. Nevertheless, the hard-sphere model should be regarded as a first-order geometrical description of the lattice response rather than a complete representation of the defect chemistry of the doped UO_2 system.

The LA-ICP-MS measurements, presented in Figure 5.13, provide complementary information on the spatial stability of the lanthanide signal relative to the uranium matrix. The measured $\text{Ln}/^{235}\text{U}$ signal ratios exhibit relatively narrow distributions for each composition, indicating a stable analytical response along the investigated ablation paths. No pronounced variations are observed over the analyzed regions that would suggest large-scale compositional heterogeneity at the spatial scale probed by the technique.

Differences in the absolute $\text{Ln}/^{235}\text{U}$ signal levels between the different lanthanides should not be interpreted directly as differences in dopant concentration. These differences reflect mostly the natural isotopic abundances of the monitored isotopes, namely ^{139}La (99.91%), ^{140}Ce (88.45%), ^{141}Pr (100%), ^{145}Nd (8.29%), and ^{155}Gd (14.80%), together with differences in elemental ICP-MS response [71]. Since the laser spot size is larger than the characteristic grain size of the pellets, each measurement samples material from several grains, reducing sensitivity to variations occurring at the scale of individual grains.

Overall, the combined chemical, microstructural, and structural characterization demonstrates that the co-precipitation and SPS processing route produces dense lanthanide-doped UO_2 materials with compositions close to their nominal targets and systematic crystallographic behaviour. The absence of detectable secondary phases, the dopant-dependent lattice parameter evolution, the agreement with the ionic-radius model, and the stable LA-ICP-MS response together support controlled incorporation and distribution of the lanthanide dopants within the UO_2 matrix.

7

Conclusion

A systematic SPS parameter map of micrometric UO_2 powder was established by varying temperature (800–1500 °C), pressure (60–160 MPa), and holding time (1–15 min). Densification increases with temperature and pressure but remains limited to approximately 93–94% TD within the investigated window. Punch displacement curves reveal a two-stage process consisting of rapid pressure-assisted particle rearrangement followed by a slower diffusion-controlled densification regime. The densification plateau at high temperature and pressure is attributed primarily to the characteristics of the starting powder, which exhibits a low specific surface area ($0.27 \text{ m}^2\text{g}^{-1}$) and a micrometric particle size of approximately $1.8 \text{ }\mu\text{m}$. These characteristics provide a relatively low surface-energy driving force for further sintering. The near-stoichiometric composition ($\text{UO}_{2.00\pm0.01}$) indicates that oxygen non-stoichiometry does not significantly influence the observed behaviour.

Lanthanide-doped UO_2 powders synthesized by wet co-precipitation generally exhibit higher specific surface areas than the powder used for the SPS mapping study, contributing to improved densification to 96–98% TD under controlled SPS conditions. ICP–MS confirms lanthanide mass fractions close to the targeted 1 wt%, while high-resolution synchrotron diffraction shows retention of the fluorite structure without detectable secondary crystalline phases. The hard-sphere model shows good agreement with the HR-PXRD-refined lattice parameters, indicating that the observed lattice parameter trends are mainly governed by cation size and charge-compensation effects. LA-ICP–MS measurements further show stable lanthanide-to-uranium signal responses along the analyzed pellet regions, with no pronounced compositional variations detected at the spatial scale probed.

Overall, this work demonstrates that densification and structural behaviour in UO_2 -based materials are governed by the combined effects of powder characteristics, chemical composition, and SPS processing parameters. Processing conditions alone do not guarantee full densification because control of precursor chemistry and powder characteristics is equally important. At the same time, the lanthanide-doped systems show that controlled incorporation of La, Ce, Pr, Nd, and Gd can be achieved while retaining the fluorite structure, with systematic lattice parameter changes governed mainly by cation size and charge-compensation effects. When these factors are considered together, SPS provides a reliable route for producing dense and structurally well-defined surrogate nuclear fuel materials.

More broadly, the results show that the complete fabrication route, from precursor synthesis and dopant incorporation to final consolidation, has a direct influence on the properties of UO_2 -based fuels. SPS enables rapid pressure-assisted consolidation and substantially shorter processing times than conventional prolonged

7. Conclusion

high-temperature sintering, while the lanthanide-doped fuels demonstrate that compositional modifications can be introduced in a controlled manner without disrupting the fluorite structure at the investigated concentrations. These findings provide useful guidance for the design and fabrication of future surrogate and advanced nuclear fuel systems with increasingly complex compositions.

Future Work

The work presented in this thesis provides the basis for future studies within the FREDMANS project, which aims to support the recycling of spent nuclear fuel and the transition towards a closed nuclear fuel cycle.

The main objective will be the synthesis and characterization of MOX fuels containing plutonium and americium together with impurity elements originating from the CHALMEX recycling process. In parallel, surrogate systems based on Ce and Nd will be fabricated to enable complementary studies without the use of heavy actinides. These studies will be used to investigate how impurity elements evolve during the different stages of fuel fabrication, from precursor synthesis and powder processing to sintering and the final fuel microstructure.

By improving the understanding of impurity behaviour during recycled fuel fabrication, these studies will provide knowledge that supports the development of advanced nuclear fuel recycling technologies and the transition towards a closed nuclear fuel cycle.

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Manuscript 1

Synthesis and structural characterization of single lanthanide-doped UO_2 prepared by co-precipitation and spark plasma sintering

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Abstract

The characterization of irradiated nuclear fuel is experimentally challenging due to its radiological hazards and complex microstructure, making simulated fuels (simfuels) valuable model systems for controlled studies of fission product behavior in UO_2 . In this study, five UO_2 -based samples doped with 1 wt% of individual lanthanides (La, Ce, Pr, Nd, and Gd) were synthesized to investigate lattice evolution and charge compensation associated with lanthanide incorporation. Precursor powders were produced by co-precipitation from uranyl nitrate and lanthanide nitrate solutions using ammonium hydroxide, followed by calcination to U_3O_8 , reduction in hydrogen to doped UO_2 , and pellet fabrication by spark plasma sintering (SPS). Structural characterization by synchrotron high-resolution powder X-ray diffraction (HR-PXRD) at the ESRF BM20 beamline confirmed single-phase fluorite UO_2 for all compositions and revealed systematic lattice parameter variations consistent with substitutional incorporation of the lanthanide dopants. The measured lattice parameters showed excellent agreement with values calculated using the hard-sphere model based on ionic radii for the fluorite structure, further supporting lanthanide incorporation and charge-compensation effects in the doped lattice. Complementary SEM observations showed dense pellet microstructures with grain sizes of approximately 1–5 μm , consistent with the high relative densities measured by helium pycnometry. LA-ICP-MS measurements showed stable $\text{Ln}/^{235}\text{U}$ signal ratios during ablation, indicating no evidence of large scale heterogeneity across the analysed pellet surfaces. These results demonstrate that the combined co-precipitation and SPS route produces structurally well-defined lanthanide-doped UO_2 materials suitable for studying dopant–matrix interactions and as potential matrix-matched reference materials for nuclear analytical applications.

1. Introduction

The analysis and characterization of irradiated nuclear fuel remains one of the most demanding challenges in nuclear materials research. Spent fuels exhibit intense gamma and neutron emissions, high radiotoxicity, and chemical complexity arising from fission product accumulation, transmutation, and irradiation-induced microstructural changes. Handling such materials requires shielded hot cells, remote manipulation, and strict radiological protocols, while experimental access is often limited by regulatory and logistical constraints.

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These factors make it difficult to isolate individual phenomena and to systematically study the specific effects of dopants, defect chemistry, and structural modifications in the UO_2 matrix [1, 2].

Simulated fuels (simfuels) provide a controlled and safe framework for investigating the behaviour of selected fission product elements in UO_2 [3, 4]. By introducing well-defined dopants into the fluorite lattice, individual chemical effects can be studied independently of the complex irradiation environment present in spent fuel. Among the most relevant dopants are lanthanides, which constitute a significant fraction of the fission product inventory and are known to influence the thermophysical and structural properties of uranium dioxide [5, 6]. Controlled incorporation of these elements therefore enables systematic investigations of dopant substitution, charge compensation mechanisms, and lattice response under well-defined laboratory conditions. Despite the extensive use of lanthanide-doped UO_2 as simfuel materials, quantitative experimental studies addressing charge compensation mechanisms and subtle lattice distortions at low dopant concentrations remain limited.

Although simfuels are frequently employed to mimic aspects of irradiated nuclear fuel, their usefulness extends beyond burnup simulation. Chemically controlled surrogate materials provide valuable model systems for studying dopant–matrix interactions in actinide oxides and for developing analytical methodologies applicable to nuclear materials. In particular, well-characterized doped UO_2 compositions can serve as matrix-matched reference materials for analytical techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), where suitable actinide-bearing calibration standards remain scarce. Such systems therefore provide both a platform for investigating the fundamental chemistry of dopant incorporation and a practical route for developing reliable analytical reference materials.

Understanding how dopants modify the UO_2 lattice requires high-precision structural characterization [7]. High-resolution powder X-ray diffraction (HR-PXRD) is particularly well suited for this purpose, as it provides the sensitivity required to detect subtle lattice parameter changes, phase segregation, or the formation of secondary oxides. In doped UO_2 systems, HR-PXRD enables direct verification of whether lanthanide ions are structurally incorporated into the fluorite lattice or form separate phases. The technique also allows the evaluation of lattice expansion and charge compensation effects associated with the substitution of trivalent lanthanide ions for U(IV) , which may induce partial oxidation of uranium in the host structure [8, 9, 10, 11]. The precision of synchrotron-based diffraction measurements makes it possible to quantify these effects even at low dopant concentrations.

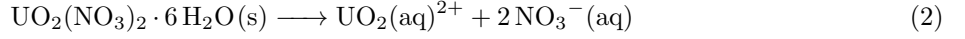
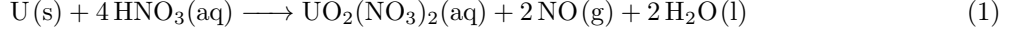
In this work, five 1 wt% lanthanide-doped UO_2 compositions (La, Ce, Pr, Nd, and Gd) were synthesized through wet chemical co-precipitation followed by thermal reduction and spark plasma sintering (SPS). A dopant concentration of 1 wt% was selected to produce measurable lattice parameter shifts while remaining within the solid-solution regime of lanthanides in the fluorite UO_2 lattice. This concentration therefore allows the structural effects of dopant incorporation and charge compensation to be evaluated while maintaining single-phase materials suitable for high-resolution diffraction analysis. The materials were investigated primarily by synchrotron HR-PXRD to verify phase purity and quantify lattice parameter variations associated with lanthanide incorporation. The measured lattice parameters were compared with values calculated using the hard-sphere ionic-radius model for the fluorite structure, in order to assess whether the observed structural response is consistent with substitutional incorporation and charge-compensation effects. Complementary microstructural characterization was performed by scanning electron microscopy (SEM), while LA-ICP-MS measurements were used to assess the analytical response of the doped materials during laser ablation.

The novelty of this work lies in combining controlled low level lanthanide doping with synchrotron HR-PXRD lattice parameter analysis and hard-sphere ionic-radius modelling to evaluate dopant incorporation in UO_2 at the 1 wt% level. By combining controlled chemical synthesis with high-resolution structural characterization, this study establishes a well defined set of lanthanide-doped UO_2 materials suitable for investigating dopant–matrix interactions and for supporting the development of matrix-matched analytical reference materials for actinide systems.

2. Experimental

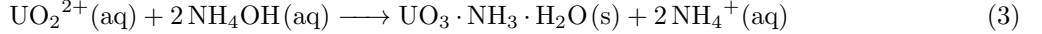
2.1. Co-precipitation

The starting material for sample fabrication was metallic uranium, which was dissolved in 69% concentrated nitric acid as shown in Equation 1. Crystals of uranyl nitrate hexahydrate were collected and dissolved in MQ-grade water (18 M Ω cm) to create a 2.1 M uranyl nitrate aqueous solution, according to the reaction shown in Equation 2.

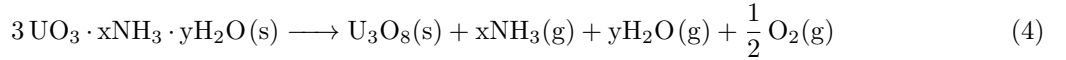


Five stock solutions, each containing a single lanthanide dopant, were prepared by dissolving the corresponding lanthanide nitrate salt in 0.1 M nitric acid. La, Pr, Nd, and Gd were dissolved from their nitrate hexahydrate salts $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% trace metals basis), while the Ce stock solution was prepared from ceric ammonium nitrate $(\text{NH}_4)_2\text{Ce}(\text{IV})(\text{NO}_3)_6$ (98.5% purity). The five doped UO_2 samples were then prepared by mixing each lanthanide solution with the uranyl nitrate solution to obtain a nominal lanthanide content of 1 wt% of the total Ln + U mass.

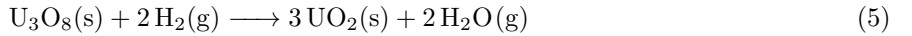
Co-precipitation was carried out by manually adding droplets of the mixed lanthanide–uranium nitrate solution into a tube containing 28-30% aqueous ammonia, $\text{NH}_3(\text{aq})$. The uranyl ion precipitation reaction is shown in Equation 3 [12]. The resulting solid precipitates were separated from the aqueous ammonia by centrifugation. The separated solids were redispersed in MQ water and recentrifuged twice to wash out excess aqueous ammonia and ammonium nitrate. The precipitated solid was finally dispersed in ethanol, poured from the centrifuge tube into a collection beaker and the ethanol was evaporated at room temperature.



The dried powders were calcined in an Entech ETF 30-50/18-S tube furnace. Both the furnace tube and sample boats used were made of alumina and the samples were calcined at 800 °C for 2 hours under air atmosphere, according to the reaction shown in Equation 4. As the precipitated UO_3 can bind crystal coordinated ammonia and water in several stoichiometries Equation 4 is written as a generic decomposition reaction [13].



The calcined powders were reduced to UO_2 using the same furnace setup as during calcination. The temperature was increased to 1200 °C and maintained for 5 hours under a flowing atmosphere of 5% H_2 and 95%Ar to reduce the U_3O_8 to UO_2 , as shown in Equation 5:



The resulting powders were collected and subdivided: 1 g was allocated for spark plasma sintering to form dense pellets, while another 1 g was reserved for ICP-MS and HR-PXRD characterization.

2.2. Spark Plasma Sintering

Five individual pellets were fabricated, each corresponding to one of the lanthanide-doped compositions (La, Ce, Pr, Nd, and Gd), allowing the structural response of the UO_2 lattice to be evaluated independently for each dopant. The sintering of the pellets was performed using Spark Plasma Sintering (SPS) at Stockholm University, a technique that enables rapid densification and precise control of processing parameters [14]. The instrument used was a Dr. Sinter 530 ET SPS unit integrated within a glovebox.

Each pellet was prepared from 1 g of powder, which was loaded into graphite pressing dies with an inner diameter of 8 mm and height of 30 mm. The sintering temperature was set to 1200 °C, reached using a heating ramp of 100 °C/min. An uniaxial pressure of 100 MPa was applied, and the holding time at peak temperature was 15 minutes [14, 15]. Following sintering, the samples were rapidly cooled under vacuum and subsequently extracted from the dies using a hydraulic press.

2.3. Powder ICP-MS Analysis

ICP-MS analysis was carried out to determine the lanthanide dopant concentration in each sample. Part of each Ln-doped powder was dissolved in 69% nitric acid and subsequently diluted in 0.5 M nitric acid containing 1 ppb Bi, which was used as an internal standard during the ICP-MS measurements. All measurements were performed using a Thermo Scientific iCAP Q ICP-MS instrument. One dissolved sample was analyzed for each composition, and the instrument performed 10 replicate readings for each sample.

2.4. Powder and pellet characterization (BET and SEM)

The specific surface area of the synthesized powders was determined by krypton adsorption using a Micromeritics ASAP 2020 surface area analyzer. Prior to the measurements, the powders were degassed under vacuum at 300 °C to remove adsorbed moisture and volatile species. Following the degassing step, krypton adsorption-desorption isotherms were recorded at liquid nitrogen temperature. The specific surface area was subsequently calculated using the Brunauer-Emmett-Teller (BET) method.

The morphology of the starting powders was investigated by scanning electron microscopy (SEM) using a FEI Quanta ESEM instrument. A small amount of powder was dispersed onto conductive carbon tape attached to an aluminum sample stub. Micrographs were collected at several magnifications in order to evaluate particle morphology and the degree of agglomeration.

Scanning electron microscopy (SEM) was also used to evaluate the homogeneity and grain size of selected sintered UO₂-based pellets. The samples were first mounted in epoxy holders and subsequently polished using Struers silicon carbide foils of decreasing grit size, followed by DiaPro diamond suspension down to 1 µm. The sizes of the grains were estimated from the SEM images using ImageJ analysis software [16].

2.5. High-resolution powder diffraction (HR-PXRD)

To investigate crystallographic changes in the UO₂ matrix induced by lanthanide doping, high-resolution powder diffraction (HR-PXRD) analysis was performed. Because the dopant concentration was only 1 wt%, close to the detection limit of conventional laboratory XRD, the use of synchrotron-based HR-PXRD was essential to resolve subtle lattice distortions and verify the absence of minor secondary phases.

Data were collected on the XRD-1 diffractometer of the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France [17]. The energy of the incoming synchrotron radiation was calibrated with a Y metal foil and set to 17038 eV ($\lambda = 0.727692$ Å). The beam was focused to a size of 150×150 µm². The samples were filled in borosilicate glass capillaries (Hilgenberg) of 0.3 mm diameter. HR-PXRD data were collected in transmission mode with an Eiger CdTe 500k detector (Dectris) and integrated using a dedicated Python code based on PyFAI routines adapted to treat series of images collected as a function of 2θ [18]. The data were analyzed with the GSAS-II program in order to extract structural information and to identify possible minor secondary phases [19].

From each of the five lanthanide-doped UO₂ powder samples, approximately 10 mg were extracted and mixed with glass powder to a dilution of 30 mol%. This dilution was done to reduce X-ray self-absorption effects from UO₂ and to improve sample homogeneity. One additional sample of pure UO₂ was fabricated and used for reference measurements.

The mixed powders were carefully loaded into ultra-thin borosilicate capillaries with an inner diameter of 0.3 mm. The fragile glass capillaries, which contained radioactive material, were placed inside a Kapton tube for mechanical protection. The ends of the tubes were sealed with epoxy resin to prevent contamination and ensure stability during synchrotron analysis. A brass pin was inserted at one end of each Kapton tube to facilitate mounting on the HR-PXRD goniometer.

2.6. Laser Ablation ICP-MS

Laser ablation ICP-MS measurements were performed at Studsvik Nuclear AB using a modified NWR 213 laser ablation system (Elemental Scientific Lasers LLC, Bozeman, MT, USA), designed for use with radioactive samples in a shielded hot cell. The ablation chamber was connected to a PerkinElmer NexION 350D ICP-MS via a high-purity helium gas flow, which carried the dry aerosol generated during ablation.

The system uses a single quadrupole with a resolution of 0.7 amu, which does not resolve monoatomic isobaric interference, and these are reported collectively.

To protect the detector and improve sensitivity to trace components, the intense ^{238}U signal was suppressed by 99.98% using the instrument’s quadrupole ion deflector. Laser line scans were performed over a distance of 5000 μm using a $20\times 20\ \mu\text{m}$ spot size, 25 $\mu\text{m}/\text{s}$ scan speed, 20 Hz pulse rate, and 25% laser power. A single line scan was performed on each sample. The pellets, each representing a different lanthanide-doped composition, remained stationary behind a laser-transparent window, while the motor-driven laser platform performed the scan [20].

3. Results

3.1. Powder ICP-MS analysis results

The chemical composition of the synthesized materials was verified by ICP-MS analysis, and the measured elemental concentrations are summarized in Table 1. The measurements were performed on 100k-fold diluted solutions, and the elemental concentrations are reported in nM. The lanthanide mass fraction was calculated from the measured molar concentrations according to $w_{\text{Ln}} = c_{\text{Ln}}M_{\text{Ln}}/(c_{\text{Ln}}M_{\text{Ln}} + c_{\text{U}}M_{\text{U}}) \times 100$, where c denotes the molar concentration and M the molar mass. The common dilution factor therefore cancels out and does not affect the calculated composition. Calibration standards were used to account for differences in elemental ICP-MS sensitivity between uranium and the lanthanides.

Table 1: ICP-MS results of the diluted dissolved powder samples, showing the measured lanthanide and uranium concentrations in nM and the corresponding calculated lanthanide mass fractions. One ICP-MS measurement was performed for each dissolved sample. The reported uncertainties are derived from the reported RSD values and represent instrumental repeatability. The measured compositions are close to the nominal target of 1 wt% lanthanide.

Dopant	Ln (nM)	^{238}U (nM)	Ln (wt%)
La	2.76 ± 0.07	139.16 ± 2.66	1.15 ± 0.04
Ce	3.00 ± 0.04	159.12 ± 2.66	1.10 ± 0.02
Pr	2.90 ± 0.09	145.95 ± 2.73	1.16 ± 0.04
Nd	2.75 ± 0.07	157.46 ± 2.25	1.05 ± 0.03
Gd	3.13 ± 0.08	173.75 ± 2.21	1.18 ± 0.03

3.2. Specific surface area of starting powders (BET)

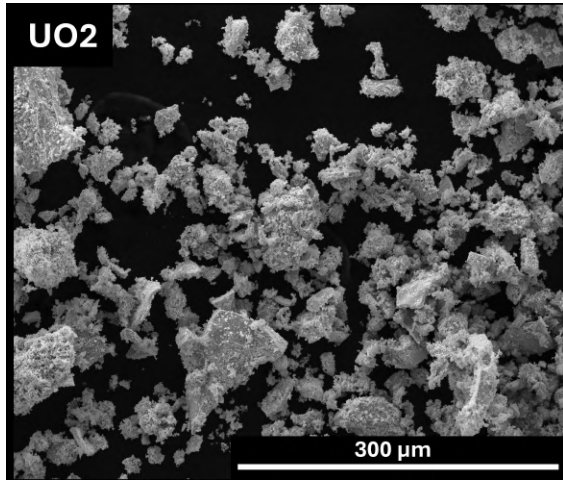
The measured BET specific surface areas for the synthesized powders are summarized in Table 2.

Table 2: BET specific surface areas of pure and lanthanide-doped UO_2 precursor powders measured by krypton adsorption. All samples exhibit similar surface areas, except the 1 wt% Nd-doped powder, which shows a significantly lower value.

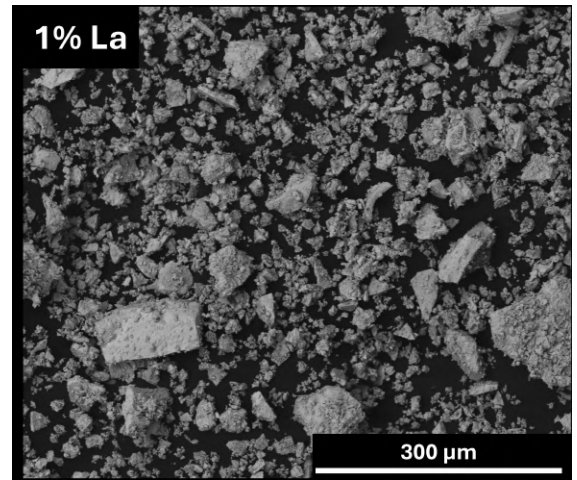
Sample	Surface area (m^2/g)
Pure UO_2	1.504 ± 0.004
1 wt% La- UO_2	1.463 ± 0.009
1 wt% Ce- UO_2	1.303 ± 0.003
1 wt% Pr- UO_2	1.541 ± 0.008
1 wt% Nd- UO_2	0.549 ± 0.001
1 wt% Gd- UO_2	1.594 ± 0.005

3.3. SEM analysis of starting powders

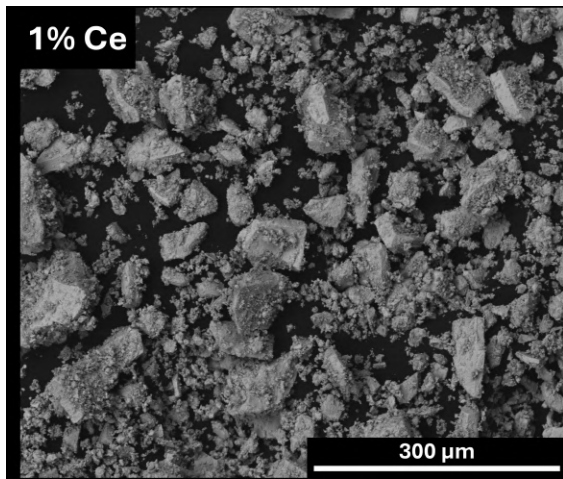
The morphology of the synthesized starting powders was examined by SEM prior to pellet fabrication. The images of the reference UO_2 powder and the lanthanide-doped powders are shown in Figure 1.



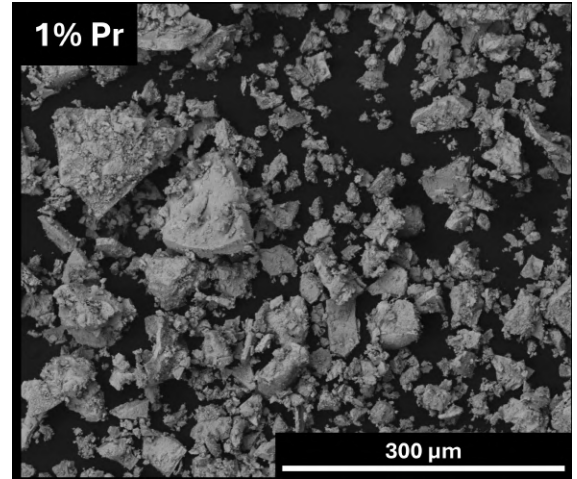
(a) Pure UO_2 powder.



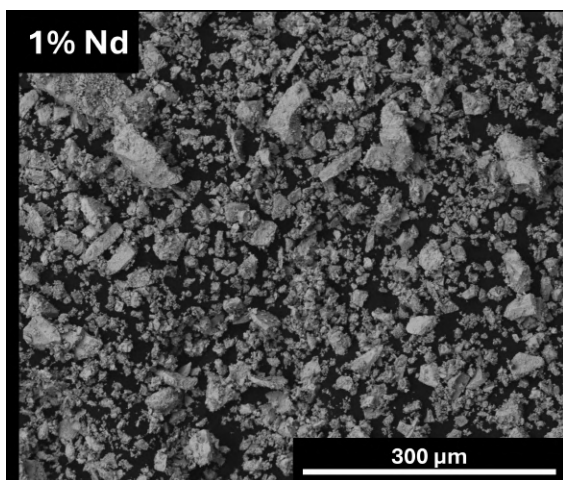
(b) 1 wt% La-doped UO_2 powder.



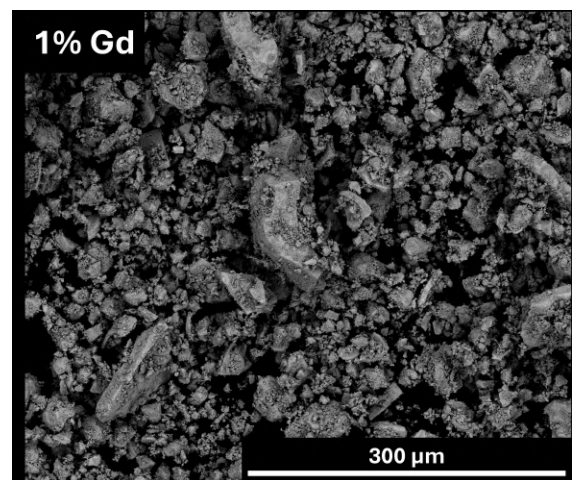
(c) 1 wt% Ce-doped UO_2 powder.



(d) 1 wt% Pr-doped UO_2 powder.



(e) 1 wt% Nd-doped UO_2 powder.



(f) 1 wt% Gd-doped UO_2 powder.

Figure 1: SEM images of pure and lanthanide-doped UO_2 precursor powders after calcination and reduction, showing irregular morphologies and similar agglomerated structures across the compositions.

All powders exhibit irregular particle morphologies with visible agglomeration at the micrometre scale. The micrographs show broadly comparable morphological characteristics for the undoped and lanthanide-doped powders.

3.4. Pellet density measurements

The densities of the five lanthanide-doped UO_2 pellets, produced by Spark Plasma Sintering (SPS), were measured using helium pycnometry. The instrument used was a Micromeritics AccuPyc II 1340. The measured densities of the pellets along with their uncertainties and the relative densities are presented in Table 3. The relative density is defined as the ratio of the measured density to the theoretical value (10.97 g/cm^3) [15]. As the doping level is only 1 wt%, the theoretical density of pure UO_2 was used as a common reference value for all compositions to compare their densification behaviour.

Table 3: Helium pycnometry results for spark plasma sintered lanthanide-doped UO_2 pellets, showing measured densities and corresponding relative densities based on the theoretical density of pure UO_2 . No significant differences are observed between the different lanthanide dopants.

Dopant	Density (g/cm^3)	Relative Density (%)
1 wt% Ce	10.682 ± 0.009	97.4
1 wt% Nd	10.667 ± 0.042	97.2
1 wt% La	10.763 ± 0.017	98.1
1 wt% Pr	10.591 ± 0.034	96.5
1 wt% Gd	10.627 ± 0.004	96.9

3.5. Pellets SEM results

SEM analysis was carried out on two representative samples, specifically the 1 wt% La- and 1 wt% Pr-doped UO_2 pellets, to evaluate the grain structure and porosity. High-magnification micrographs of the sintered surfaces are shown in Figure 2. The grain morphology appears well-sintered, with residual porosity visible in both samples, while the grain size distributions and porosity values are summarized in Table 4.

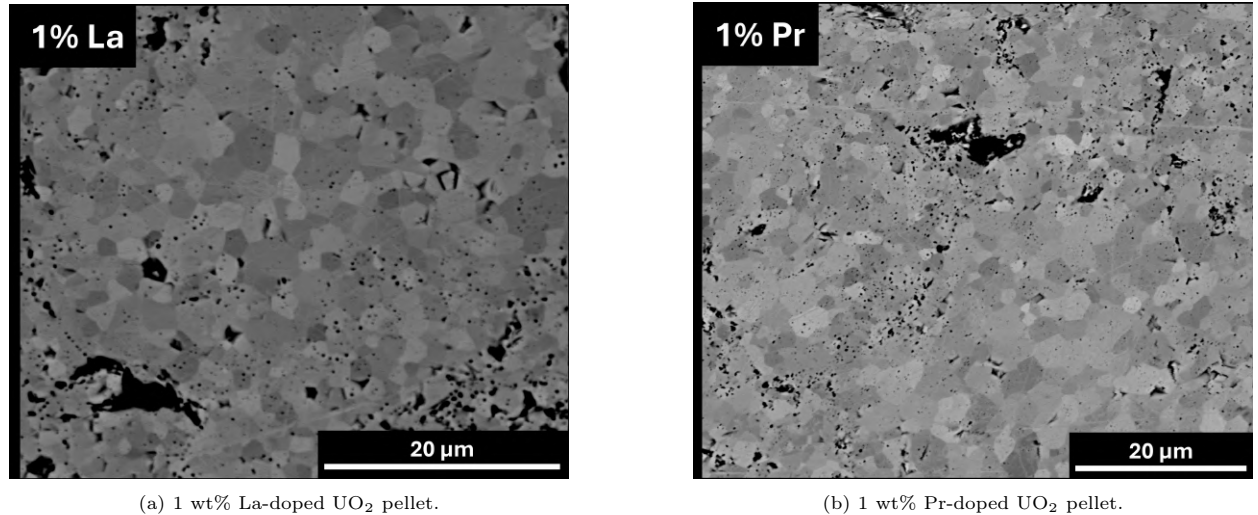


Figure 2: SEM images of 1 wt% La- and 1 wt% Pr-doped UO_2 pellets after polishing, showing well-sintered microstructures with residual porosity.

Table 4: Microstructural properties of 1 wt% La- and 1 wt% Pr-doped UO_2 samples.

	1 wt% La	1 wt% Pr
Average grain size (μm)	2.03 ± 0.06	2.53 ± 0.87
Grain size range (μm)	0.9–3.7	0.9–5.1
Porosity (%)	6.33	4.12

Grain size analysis with ImageJ software revealed average sizes of $2.03 \pm 0.06 \mu\text{m}$ for La-doped and $2.53 \pm 0.87 \mu\text{m}$ for Pr-doped samples, with overall grain size ranges of 0.9–3.7 μm and 0.9–5.1 μm , respectively. These values are consistent with the expected microstructure of UO_2 pellets synthesized via SPS [21].

3.6. High-resolution powder diffraction and lattice parameter modelling

Refinement of the HR-PXRD data confirmed a single-phase fluorite UO_2 structure in all samples, with no secondary phases detected. The lattice parameters determined using GSAS-II are presented in Table 5.

Table 5: Refined lattice parameters obtained from HR-PXRD analysis using GSAS-II.

Composition	a_{meas} ($\text{\AA}$)
Pure UO_2	5.47120(6)
1 wt% La	5.47198(3)
1 wt% Ce	5.46970(3)
1 wt% Pr	5.46969(3)
1 wt% Nd	5.46983(3)
1 wt% Gd	5.46790(3)

The experimentally measured lattice parameter of pure UO_2 of 5.47120 $\text{\AA}$ obtained in this study is in excellent agreement with the literature value of 5.47127 $\text{\AA}$ [22].

To evaluate whether the measured lattice parameters are consistent with substitutional lanthanide incorporation, the hard-sphere model based on ionic radii for the fluorite structure was applied [10]. In this model, the lattice parameter is estimated from the average cation radius and the oxygen anion radius according to Equation 6.

$$a_{\text{calc}} = \frac{4}{\sqrt{3}} (\bar{r}_c + r_{\text{O}^{2-}}), \quad (6)$$

where a_{calc} is the calculated lattice parameter, $\bar{r}_c$ is the average cation radius, and $r_{\text{O}^{2-}}$ is the ionic radius of oxygen. The average cation radius was calculated from the fractional occupancies of the cation sublattice:

$$\bar{r}_c = (X_{\text{U}^{4+}})(r_{\text{U}^{4+}}) + (X_{\text{U}^{5+}})(r_{\text{U}^{5+}}) + (X_{\text{Ln}})(r_{\text{Ln}}), \quad (7)$$

where X_i and r_i are the cation fraction and ionic radius of species i , respectively. The lanthanide cation fraction x was calculated from the ICP–MS mass concentrations after conversion to molar fractions:

$$x = \frac{m_{\text{Ln}}/M_{\text{Ln}}}{m_{\text{Ln}}/M_{\text{Ln}} + m_{\text{U}}/M_{\text{U}}}, \quad (8)$$

where m_{Ln} and m_{U} are the ICP–MS measured mass concentrations of the lanthanide and uranium, respectively, and M_{Ln} and M_{U} are their corresponding molar masses.

For La, Pr, Nd, and Gd, the lanthanides were treated as trivalent and charge compensation was assumed to occur through oxidation of an equivalent fraction of U(IV) to U(V). Therefore,

$$X_{\text{Ln}^{3+}} = x, \quad X_{\text{U}^{5+}} = x, \quad X_{\text{U}^{4+}} = 1 - 2x. \quad (9)$$

Substitution into Eq. 6 gives:

$$a_{\text{calc}} = \frac{4}{\sqrt{3}} [r_{\text{O}^{2-}} + (1 - 2x)r_{\text{U}^{4+}} + xr_{\text{U}^{5+}} + xr_{\text{Ln}^{3+}}]. \quad (10)$$

For the Ce-doped sample, cerium was treated as tetravalent Ce(IV) because the synthesis used ceric ammonium nitrate $((\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6)$, a Ce(IV) precursor. Also, the measured lattice parameter shows a contraction relative to pure UO_2 , consistent with substitution by the smaller Ce(IV) ion. Therefore, no U(V) charge compensation was included. In this case,

$$X_{\text{Ce}^{4+}} = x, \quad X_{\text{U}^{4+}} = 1 - x, \quad (11)$$

and the calculated lattice parameter is given by:

$$a_{\text{calc}} = \frac{4}{\sqrt{3}} [r_{\text{O}^{2-}} + (1 - x)r_{\text{U}^{4+}} + xr_{\text{Ce}^{4+}}]. \quad (12)$$

The ionic radii used in the calculations are presented in Table 6 as reported by Ohmichi et al. and Shannon [10, 23]. The oxygen ionic radius was taken as 1.368 Å, obtained from the fluorite geometry of stoichiometric UO_2 using $a_{\text{UO}_2} = 5.47127$ Å and $r_{\text{U}^{4+}} = 1.001$ Å.

Table 6: Ionic radii used in the geometrical ionic-radius model. Cation radii are given for CN = 8 [10, 23].

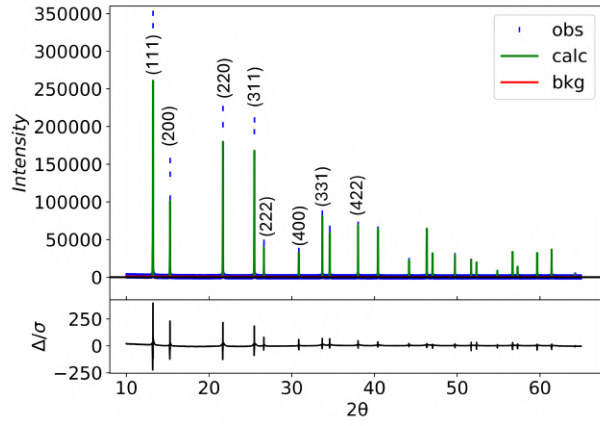
Ion	Ionic Radius (Å)
O^{2-}	1.368
U^{4+}	1.001
U^{5+}	0.880
La^{3+}	1.160
Ce^{4+}	0.970
Pr^{3+}	1.126
Nd^{3+}	1.109
Gd^{3+}	1.053

The calculated lattice parameters obtained from the ionic-radius model are compared with the experimentally refined HR-PXRD values in Table 7.

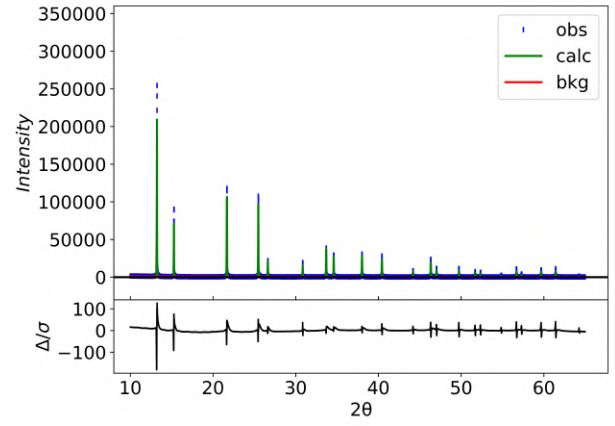
Table 7: Comparison between calculated and measured lattice parameters for pure and lanthanide-doped UO_2 , showing excellent agreement between the geometrical ionic-radius model for the fluorite lattice and the experimentally refined HR-PXRD values.

Composition	x (Ln fraction)	a_{calc} (Å)	a_{meas} (Å)	$a_{\text{meas}}/a_{\text{calc}}$
Pure UO_2	0.0000	5.47097	5.47120	1.00004
1 wt% La	0.0195	5.47268	5.47198	0.99987
1 wt% Ce	0.0185	5.46965	5.46970	1.00001
1 wt% Pr	0.0195	5.47115	5.46969	0.99973
1 wt% Nd	0.0171	5.47046	5.46983	0.99989
1 wt% Gd	0.0177	5.46815	5.46790	0.99995

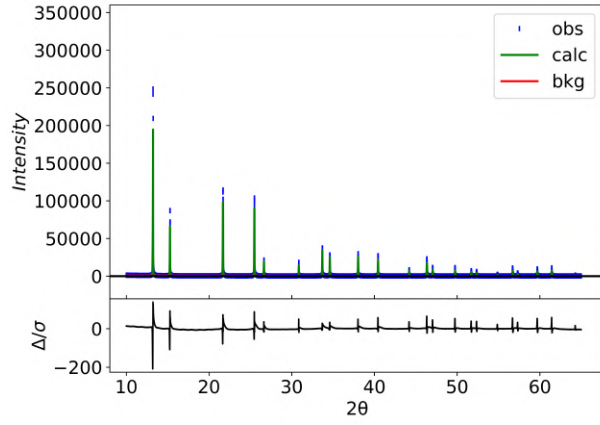
The calculated lattice parameters show excellent agreement with the experimentally refined HR-PXRD values, with $a_{\text{meas}}/a_{\text{calc}}$ ratios close to unity for all compositions. Another important observation from the HR-PXRD analysis is the absence of any secondary phases in all the doped samples. As shown in Figure 3, all diffraction patterns are consistent with single-phase fluorite UO_2 .



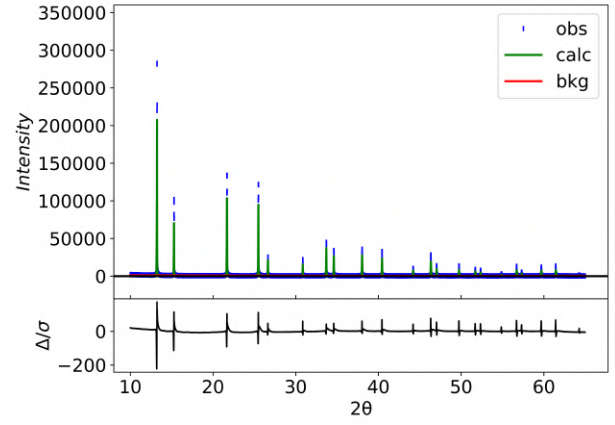
(a) Pure UO_2 .



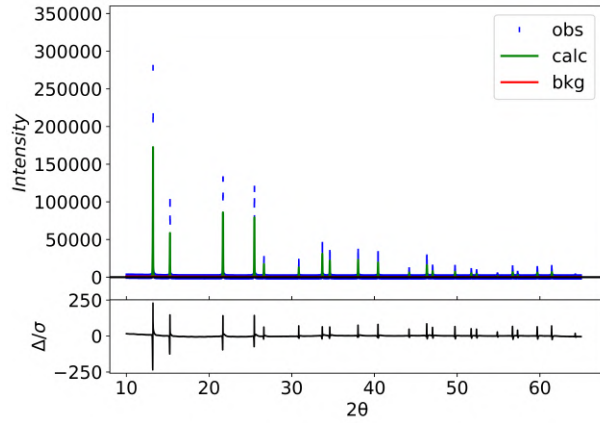
(b) 1 wt% La-doped UO_2 .



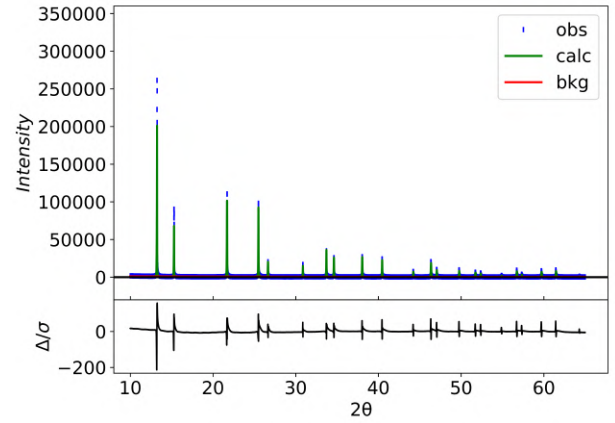
(c) 1 wt% Ce-doped UO_2 .



(d) 1 wt% Pr-doped UO_2 .



(e) 1 wt% Nd-doped UO_2 .



(f) 1 wt% Gd-doped UO_2 .

Figure 3: Rietveld refinements of HR-PXRD patterns for pure and lanthanide-doped UO_2 samples, confirming single-phase fluorite structures without detectable secondary phases. The principal crystallographic planes are indexed in the pure UO_2 pattern to indicate the characteristic reflections of the fluorite structure. In the legend, obs represents the observed diffraction pattern, calc the calculated Rietveld profile, and bkg the fitted background. The lower panel shows the normalized difference between the observed and calculated intensities, expressed as Δ/σ .

3.7. Laser ablation results

Laser ablation ICP–MS measurements were performed to evaluate the lanthanide signal response relative to the uranium matrix in the UO_2 pellets. The lanthanide-to-uranium signal ratios ($\text{Ln}/^{235}\text{U}$) were calculated from the measured ion intensities of the selected lanthanide isotopes and ^{235}U .

Figure 4 presents box-plot distributions of the $\text{Ln}/^{235}\text{U}$ signal ratios obtained during the LA-ICP-MS measurements for the five lanthanide-doped pellets (La, Ce, Pr, Nd, and Gd). Each box summarizes the distribution of signal ratios recorded along the ablation paths. The boxes represent the interquartile range with the central line corresponding to the median value, and the whiskers indicating the overall spread of the measurements.

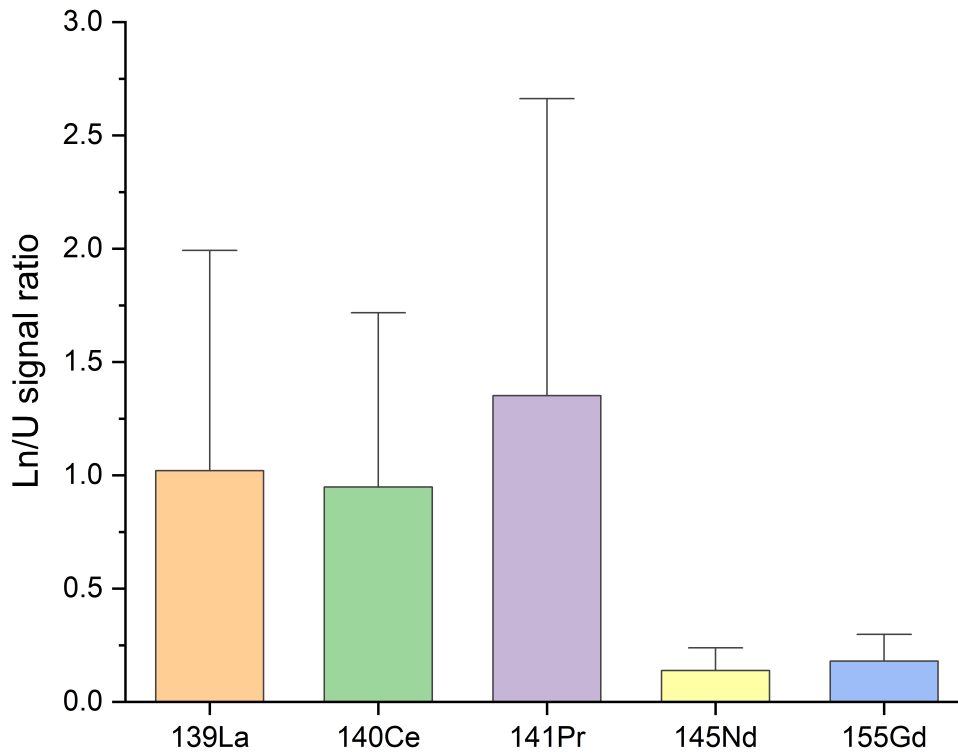


Figure 4: Box-plot distributions of $\text{Ln}/^{235}\text{U}$ signal ratios obtained during LA-ICP-MS measurements, showing consistent response across the analyzed pellet surfaces. Each box represents the interquartile range of the measured signal ratios, the central line indicates the median, and the whiskers show the overall spread of the data. Differences in mean signal levels between the lanthanides reflect the natural isotopic abundances of the monitored isotopes, while the spread within each distribution reflects signal fluctuations along the ablation path.

4. Discussion

The results demonstrate that the co-precipitation route combined with spark plasma sintering provides a reliable method for producing chemically controlled lanthanide-doped UO_2 materials. The ICP–MS measurements show lanthanide mass fractions consistently close to the targeted 1 wt% level as shown in Table 1, confirming that the wet chemical synthesis allows accurate control of dopant incorporation during precursor preparation. Such compositional reproducibility is essential when studying substitutional effects in actinide oxides, as even small deviations in dopant concentration can influence lattice parameters and defect chemistry.

The characteristics of the precursor powders provide additional insight into the processing behaviour of the materials. BET measurements yielded specific surface areas between approximately 1.3 and 1.6 m^2/g for the pure UO_2 and most lanthanide-doped powders, as presented in Table 2. The Nd-doped powder was the clear exception, exhibiting a substantially lower surface area of 0.55 m^2/g . The lower specific surface area of the Nd-doped powder is most likely associated with batch-to-batch variations during powder processing rather than with a specific effect of Nd incorporation. Since each composition was precipitated and subsequently reduced separately, small differences in precipitation or thermal-treatment conditions could influence particle size, agglomeration, and accessible surface area. Previous studies have shown that uranium precursor powder properties are sensitive to precipitation and reduction conditions [24, 25, 26].

The SEM observations, shown in Figure 1, reveal irregular particles forming large-scale agglomerates. The different lanthanide-doped powders exhibited broadly similar morphologies, with only minor qualitative variations in agglomerate size and compactness and no clearly distinct morphology associated with a specific dopant. These results indicate that the powders consist of relatively coarse primary particles produced during the precipitation, calcination, and reduction steps. Such morphologies are typical for chemically precipitated uranium oxide systems subjected to high-temperature thermal treatment [27]. Although the powders did not possess particularly high surface areas, their morphology was still suitable for consolidation by SPS, as demonstrated by the high final pellet densities.

The densification behaviour of the pellets confirms the effectiveness of the SPS processing route. Helium pycnometry measurements, presented in Table 3, reveal relative densities between 96.5 % and 98.1 % of the theoretical density of UO_2 . These values are consistent with previously reported densities for UO_2 pellets produced by spark plasma sintering [15, 28]. The SEM observations of the pellets’ surfaces, as presented in Figure 2, reveal well-developed grains together with residual porosity. Considering the particle size and the agglomeration of the precursor powders, the efficient densification can be attributed to the simultaneous application of pressure and rapid heating during SPS, which promotes particle rearrangement and diffusion processes [29]. The resulting microstructure therefore provides dense pellets with stable grain structures suitable for structural characterization.

The HR-PXRD analysis provides the most direct insight into the structural effects of lanthanide incorporation in the UO_2 lattice. For all compositions investigated, the diffraction patterns are fully consistent with the fluorite UO_2 structure and no additional diffraction peaks attributable to secondary phases were detected, as shown in Figure 3. This observation strongly supports that the lanthanide dopants are structurally incorporated into the host lattice rather than forming segregated oxide phases. The refined lattice parameter obtained for the reference UO_2 sample agrees closely with the literature value for stoichiometric UO_2 , indicating that the synthesis and reduction procedures produced material with minimal deviation from the expected oxidation state [22].

Systematic variations in the refined lattice parameters are observed across the lanthanide series, as presented in Table 5. The La-doped sample exhibits a slight lattice expansion relative to pure UO_2 , consistent with the large ionic radius of La(III) dominating over the contraction contribution associated with charge compensation. In contrast, the Ce-, Pr-, Nd-, and Gd-doped samples exhibit smaller lattice parameters. For the Ce-doped material, the lattice contraction is consistent with the presence of Ce(IV), which has a smaller ionic radius than both Ce(III) and U(IV) in eightfold coordination [23]. For the remaining trivalent lanthanides, the observed changes reflect the combined effects of ionic size and charge compensation within the fluorite lattice.

The calculated lattice parameters obtained using the hard-sphere model show excellent agreement with the experimentally refined HR-PXRD values. This agreement demonstrates that, despite its simplicity, the fluorite hard-sphere model captures the dominant contribution of cation size and charge compensation to the measured lattice parameter trends [10, 11]. For La, Pr, Nd, and Gd, the calculation assumes trivalent lanthanide substitution accompanied by charge compensation through oxidation of an equivalent fraction of U(IV) to U(V). For Ce, the dopant is treated as Ce(IV), consistent with the Ce(IV) precursor chemistry and the observed lattice contraction; therefore, no U(V) charge compensation is included.

The close agreement between calculated and measured lattice parameters is significant because the lattice shifts induced by 1 wt% lanthanide substitution are very small and would be difficult to resolve reliably using conventional laboratory XRD. The use of synchrotron HR-PXRD at ESRF therefore provides the precision required to distinguish subtle dopant dependent lattice variations and to test the ionic-radius-based structural model against experimentally refined lattice parameters. Overall, the comparison supports substitutional incorporation of the lanthanides within the fluorite UO_2 lattice and shows that the measured lattice parameter evolution is primarily governed by effective cation radii and charge-compensation effects.

Laser ablation ICP–MS measurements, presented in Figure 4, provided complementary information on the analytical response of the lanthanide dopants within the UO_2 matrix. The distributions of the measured $\text{Ln}/^{235}\text{U}$ signal ratios show consistent median values and relatively narrow interquartile ranges for each composition, indicating consistent analytical behaviour during laser ablation. Differences in the mean signal levels between the elements reflect mostly variations in the natural isotopic abundances of the monitored isotopes, namely ^{139}La (99.91%), ^{140}Ce (88.45%), ^{141}Pr (100%), ^{145}Nd (8.29%), and ^{155}Gd (14.80%), rather than differences in dopant incorporation [30]. Considering that the laser spot size is significantly larger than the average grain size of the pellets, each ablation pulse samples a large number of grains simultaneously, which reduces the influence of local microstructural variations on the measured signal ratios. The spread within each distribution reflects signal fluctuations during the LA-ICP–MS line scan and therefore is considered relative to the corresponding mean signal level.

Taken together, the structural and microstructural results demonstrate that the co-precipitation and SPS processing route yields dense, well-defined lanthanide-doped UO_2 materials with controlled compositions and systematic lattice behaviour. The absence of detectable secondary phases, the dopant-dependent lattice parameter evolution, and the agreement with the hard-sphere ionic-radius model strongly support substitutional incorporation of the lanthanides within the fluorite lattice. These characteristics make the synthesized materials suitable both for investigating dopant–matrix interactions in UO_2 and for serving as well-defined actinide-bearing reference materials in analytical applications.

5. Conclusions

The combined co-precipitation and spark plasma sintering (SPS) route successfully produced dense, phase-pure lanthanide-doped UO_2 pellets with dopant concentrations closely matching the targeted 1 wt% compositions. Synchrotron HR-PXRD analysis confirmed that all samples retain the fluorite UO_2 structure and exhibit systematic lattice parameter variations consistent with lanthanide incorporation into the UO_2 lattice. The measured lattice parameters showed excellent agreement with values calculated using a geometrical ionic-radius model for the fluorite structure, supporting substitutional incorporation of the lanthanide dopants and charge-compensation effects in the doped lattice. Complementary LA-ICP–MS measurements showed consistent analytical behaviour during laser ablation and no evidence of large-scale compositional heterogeneity at the spatial scale probed by the technique.

Overall, the absence of secondary phases and the systematic lattice parameter evolution across the lanthanide series demonstrate solid-solution formation for all compositions at the 1 wt% level. These results provide strong evidence that the lanthanides are incorporated within the fluorite lattice and that the structural response can be described primarily by effective cation radii and charge compensation. The synthesized materials are therefore chemically and structurally robust, making them suitable both as model systems for investigating dopant–matrix interactions in UO_2 and as potential matrix-matched reference materials for analytical studies of actinide-bearing systems.

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Manuscript 2

Densification limits of low surface area UO_2 during spark plasma sintering

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Abstract

A systematic Spark Plasma Sintering (SPS) study was conducted to establish a pressure–temperature–time processing map for low surface area UO_2 powder. The starting powder was characterized by X-ray diffraction, BET surface area analysis, and scanning electron microscopy. XRD confirmed a near-stoichiometric composition of $\text{UO}_{2.00\pm0.01}$, while the powder exhibited a low specific surface area ($0.27 \text{ m}^2\text{g}^{-1}$) and a mean particle size of $1.8 \mu\text{m}$, indicating a coarse morphology. A series of 35 pellets were sintered over a temperature range of 800–1500 °C, pressures of 60–160 MPa, and holding times between 1 and 15 min. Relative densities up to approximately 93–94% of theoretical density were achieved. Punch displacement analysis revealed a two-stage densification mechanism consisting of rapid pressure-assisted particle rearrangement followed by diffusion-controlled pore elimination. While increasing temperature and pressure enhanced densification, a clear plateau was observed beyond 1300–1400 °C and above 100–120 MPa. Holding time had a limited influence within the investigated range. The results demonstrate that densification under the present SPS conditions is initially mechanically assisted but ultimately diffusion-limited. This work shows that, for low surface area UO_2 powders, densification is limited to approximately 93–94% of theoretical density, regardless of further increases in temperature or pressure.

1. Introduction

Uranium dioxide (UO_2) is the most widely used nuclear fuel in commercial power reactors, particularly in Generation III light-water reactor systems. The fabrication of UO_2 fuel pellets involves several processing steps, among which the sintering stage plays a critical role in determining the final microstructure and density of the fuel [1]. In conventional industrial fabrication routes, UO_2 pellets are typically sintered for several hours at temperatures approaching 1700 °C to achieve densities close to the theoretical value.

Alternative sintering techniques have been explored to reduce both the thermal energy consumption and processing time associated with conventional sintering. One favorable candidate, spark plasma sintering (SPS), applies simultaneous uniaxial pressure and rapid heating, enabling fast densification at comparatively lower temperatures and shorter dwell times [2, 3]. SPS is widely used in materials research and offers precise and independent control of key sintering parameters, including temperature, pressure, and holding time [4]. Despite these advantages, its application to nuclear fuel fabrication remains largely limited to laboratory-scale investigations. Consequently, SPS is often employed as a research tool to study sintering mechanisms and parameter effects rather than as a fully established industrial fabrication route.

Previous studies on SPS of UO_2 have provided valuable insights into densification mechanisms and processing conditions [5, 6, 7, 8, 9, 10]. However, systematic investigations aimed at mapping the combined influence of temperature, pressure, and holding time remain limited. Moreover, the influence of the characteristics of the starting powder, particularly its specific surface area, on the achievable densification during SPS has not been extensively investigated, despite its strong impact on sintering kinetics.

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In the present work, a systematic SPS study was carried out using 35 distinct sintering conditions in order to establish a processing map for UO_2 . The primary objective is to evaluate the combined influence of temperature, uniaxial pressure, and holding time on the densification behavior of a low-surface-area UO_2 powder. Relative density measurements are used to construct a pressure–temperature map of the SPS parameter space. Particular attention is given to identifying the densification limits imposed by the low specific surface area of the starting powder.

2. Experimental

2.1. Starting UO_2 powder

The starting material was UO_2 powder supplied by Chalmers University. Prior to SPS processing, the powder was reduced in a tube furnace under an atmosphere of 95% Ar + 5% H_2 at 1400 °C for 5 h to obtain a stoichiometry as close as possible to an O/U ratio of 2.00. In order to assess the initial properties of the starting UO_2 powder prior to SPS processing, complementary surface area, phase, and microstructural characterizations were performed.

2.2. Specific surface area and particle size estimation (BET and SEM)

The specific surface area of the powder was measured by krypton adsorption using a Micromeritics ASAP 2020 surface area analyzer. Prior to the adsorption measurements, the powder was degassed at 300 °C under vacuum to remove any adsorbed moisture. After degassing, krypton adsorption–desorption isotherms were recorded at liquid nitrogen temperature. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method.

The morphology and particle size of the starting powder were examined by scanning electron microscopy using a FEI Quanta SEM (ESEM). The powder was dispersed onto a conductive carbon adhesive tape mounted on an aluminum stub. Micrographs were acquired at different magnifications to evaluate particle morphology, degree of agglomeration, and particle size distribution. Particle size was determined by direct measurement from SEM images using the ImageJ software.

2.3. X-ray diffraction (XRD)

Phase identification and crystallographic characterization of the starting powder were performed by X-ray diffraction (XRD) using a Bruker D8 Discover diffractometer. The diffraction pattern was collected over an angular range sufficient to cover the main diffraction peaks of fluorite-type UO_2 .

The diffraction data were analyzed using the GSAS-II software. The results were used to confirm phase purity and the powder’s stoichiometry. The lattice parameter was determined from peak positions, and the O/U stoichiometry was estimated by comparison with the reference value for stoichiometric UO_2 , taking into account the known dependence of lattice parameter on oxygen non-stoichiometry.

2.4. Spark plasma sintering

Pellets were sintered by Spark Plasma Sintering (SPS) at Stockholm University. The experiments were carried out using a 530 ET SPS unit installed inside a glovebox. The temperature was monitored with a pyrometer aimed at the centre of the graphite die. A 1 mm diameter aperture located at the die centre was used to facilitate pyrometer alignment and improve the reproducibility of the temperature measurement.

For each pellet, 2 g of powder was loaded into a graphite die (inner diameter: 8 mm; length: 30 mm). An initial uniaxial preload of 26 MPa was applied. The temperature was first increased to 400 °C within 2 min, and the sintering was initiated under vacuum. This step was included because the pyrometer starts logging at approximately 370 °C, and a controlled approach to this region improves the stability of temperature acquisition. The temperature was then increased to the target sintering temperature at a heating rate of 100 °C·min^{−1}.

Once the temperature reached 800 °C, the uniaxial pressure ramp was initiated with manual control and increased to the target value within approximately 2 min. After the dwell at the target temperature, the samples were rapidly cooled under vacuum and subsequently removed from the dies using a hydraulic press.

2.5. List of the fabricated pellets

The selection of SPS parameters was designed to systematically explore the pressure–temperature space relevant for UO_2 densification while maintaining a constant holding time of 5 min for the majority of experiments. The parameter combinations were distributed across the map to capture both low and high pressure regimes (60–160 MPa) and a wide temperature range (800–1500 °C). Lower temperatures were included to identify the onset of densification, while higher temperatures were used to approach the maximum achievable density under SPS conditions. Similarly, pressures were progressively increased to evaluate their contribution to particle rearrangement and compaction. This strategy allowed the construction of a pressure–temperature densification map, enabling the identification of trends, plateaus, and regions where further increases in temperature or pressure no longer resulted in significant improvements in relative density.

To place the present results in the context of previously reported SPS studies, selected data from the literature were extracted and used for comparison. In particular, density values reported for UO_2 pellets sintered at 60 MPa with temperatures of 1050, 1250, and 1450 °C were reproduced from published works [8, 9]. This comparison helps to situate the present results within the broader body of SPS studies on UO_2 .

The explored SPS parameter space was limited by the mechanical stability of the graphite tooling. The die and punches were manufactured from fine-grain graphite grade 2333 (Mersen, Compressive strength: 167 MPa), which, despite its high-temperature capability, exhibits limited mechanical strength that decreases with increasing temperature. To avoid die deformation or fracture under combined thermal and mechanical loading, the maximum applied pressure was restricted at higher temperatures. Consequently, pressures above approximately 120 MPa were not systematically applied for temperatures exceeding 1300 °C, defining the upper boundary of the investigated pressure–temperature map.

The Tables 1–2 report the pellet identifier and the corresponding SPS processing conditions.

Table 1: SPS conditions for sintered pellets (Part I).

Pellet ID	Pressure (MPa)	Temperature (°C)	Holding time (min)
1	120	1200	5
2	120	1400	5
3	120	1300	5
4	120	1350	5
5	120	1250	5
6	60	1400	5
7	60	1050	5
8	60	1250	5
9	60	1450	5
10	100	1200	5
11	60	1500	5
12	60	1200	5
13	60	1300	5
14	60	1350	5
15	100	1200	1
16	100	1200	15
17	100	1300	1
18	100	1300	5
19	100	1300	15

Table 2: SPS conditions for sintered pellets (Part II).

Pellet ID	Pressure (MPa)	Temperature (°C)	Holding time (min)
20	100	1400	1
21	100	1400	5
22	100	1400	15
23	100	1500	1
24	100	1500	5
25	100	1500	15
26	120	1500	5
27	130	1300	5
28	100	1300	5
29	100	1300	5
30	100	1400	1
31	100	1400	1
32	140	1300	5
33	150	1300	5
34	160	1300	5
35	60	800	5

2.6. Density measurements

The bulk density of the UO_2 pellets was measured using the Archimedes method. All measurements were performed using an analytical balance with a readability of four decimal places, equipped with a dedicated Archimedes measurement kit. Each pellet was weighed in air and subsequently immersed in ethanol for the buoyancy measurement. Ethanol was selected as the immersion medium to ensure good wetting of the pellet surface. For each pellet, two independent Archimedes measurements were performed to improve measurement reliability.

During immersion, the pellets were positioned on their thin side in order to facilitate the release of trapped air and to minimize the retention of gas bubbles on the pellet surface. After immersion, a waiting time of at least 2 min was systematically applied before recording the immersed weight, allowing residual air bubbles to escape from the pellet surface. The reported density values correspond to the average of the two measurements performed for each pellet.

2.7. Porosity quantification of selected pellets

From the initial dataset, four pellets were selected for microstructural porosity analysis by scanning electron microscopy (SEM). The selection aimed to represent the main regions of the SPS processing parameter space while limiting the number of samples to a manageable level for quantitative image analysis. The selection criteria were: (i) evaluation of the effect of sintering temperature at constant pressure and holding time, and (ii) evaluation of the effect of applied pressure at constant temperature and holding time.

Pellets 10, 18, and 24 were selected to form a temperature series at constant pressure and holding time. These pellets were all sintered at 100 MPa for 5 min, at temperatures of 1200 °C (pellet 10), 1300 °C (pellet 18), and 1500 °C (pellet 24), respectively. To isolate the effect of applied pressure, pellet 35, sintered at 160 MPa, 1300 °C, and a holding time of 5 min, was selected for comparison with pellet 18, which was processed at identical temperature and holding time but lower pressure. The selected pellets were manually polished using standard metallographic procedures with progressively finer abrasives and final micron diamond suspensions. Quantitative porosity analysis was conducted using ImageJ. The measured two-dimensional pore area fraction was used as an approximation of the relative porosity.

3. Results

3.1. Phase composition and stoichiometry (XRD)

The refinement of the powder X-ray diffraction data is presented in Fig.1.

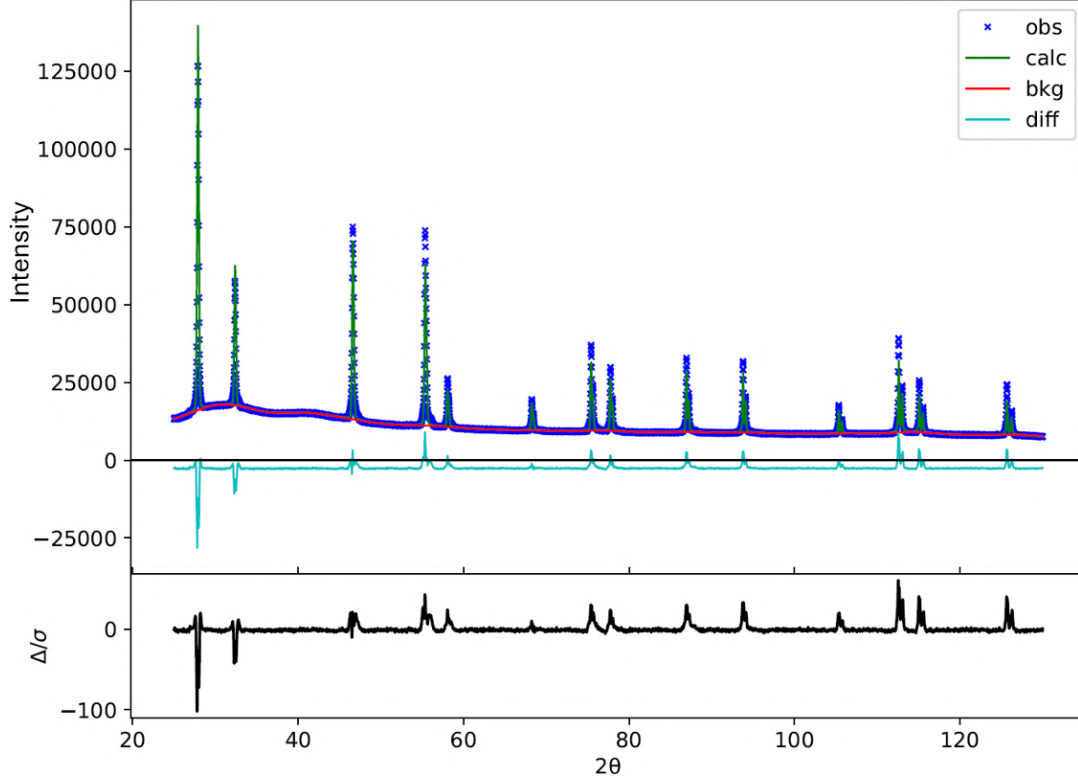


Figure 1: XRD refinement of the starting UO_2 powder showing good agreement between observed and calculated patterns. No secondary phases are detected, confirming phase purity.

The refined cubic lattice parameter was $a_{\text{meas}} = 5.4709 \text{ \AA}$. The oxygen stoichiometry was estimated using the empirical Vegard-law relation valid for near-stoichiometric UO_2 , $a(x) = a_0 - kx$, where $a_0 = 5.47127 \text{ \AA}$ is the lattice parameter of stoichiometric UO_2 at room temperature and $k = 0.13 \text{ \AA}$ per oxygen atom [11]. The lattice parameter difference $\Delta a = a_0 - a_{\text{meas}} = 5.47127 - 5.47090 = 0.00037 \text{ \AA}$ yields an oxygen deviation $x = \Delta a/k = 0.00037/0.13 = 2.85 \times 10^{-3}$, corresponding to a composition of $\text{UO}_{2+0.0029} \approx \text{UO}_{2.003}$.

Considering the typical uncertainty of laboratory Bragg–Brentano measurements ($\pm 0.001\text{--}0.002 \text{ \AA}$), the associated uncertainty in oxygen content is approximately ± 0.01 , and the material is therefore best described as $\text{UO}_{2.00 \pm 0.01}$.

These results indicate that the sample is essentially stoichiometric UO_2 , with no statistically significant oxygen non-stoichiometry detectable by laboratory X-ray diffraction.

3.2. Specific surface area and morphology of the starting powder

The krypton adsorption measurements yielded a specific surface area of:

$$S_{\text{BET}} = 0.27 \text{ m}^2\text{g}^{-1} \quad (1)$$

The SEM observations revealed a homogeneous powder composed predominantly of well-defined coarse particles with limited agglomeration. The particles exhibit similar morphology across the sample, with only a minor fraction forming small agglomerates. Direct measurements from SEM micrographs yield a mean particle size of 1.8 μm , with a size distribution ranging from approximately 0.5 to 5 μm . The morphology is consistent across different regions, indicating good homogeneity of the starting powder. These observations are consistent with the low BET specific surface area and confirm the coarse particle nature of the powder. In the next Figure 2 the SEM images are presented.

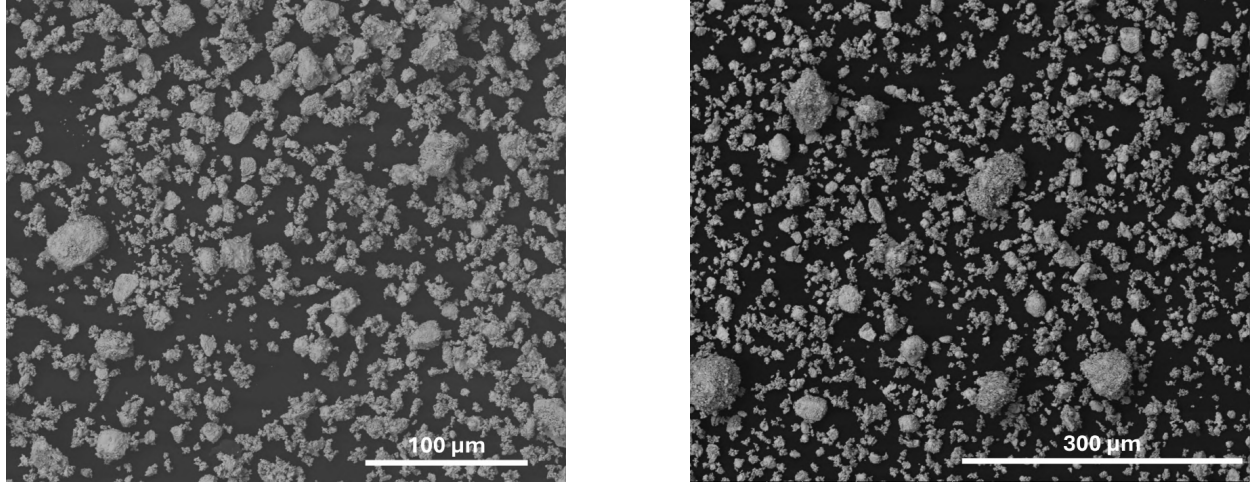


Figure 2: SEM micrographs of the starting UO_2 powder showing coarse particles with limited agglomeration.

3.3. Density measurement results

The sintering conditions and corresponding density measurements for all UO_2 pellets investigated in this study are summarized in Table 3 and Table 4. The table reports the applied pressure, sintering temperature, holding time, measured bulk density, and the relative density expressed as a percentage of the theoretical density. The listed values represent the average of repeated Archimedes measurements, with the associated standard deviation provided to quantify measurement reproducibility. This dataset forms the basis for the subsequent analysis of temperature, pressure, and holding-time effects on densification. The relative density is defined as the ratio of the measured density to the theoretical value (10.97 g/cm^3) [12].

Table 3: Bulk density and relative density of SPS-sintered UO_2 pellets (Part I).

Pellet ID	Pressure (MPa)	Temperature ($^{\circ}\text{C}$)	Time (min)	Density (g/cm^3)	TD (%)
1	120	1200	5	9.83 ± 0.08	89.65 ± 0.74
2	120	1400	5	10.18 ± 0.03	92.77 ± 0.27
3	120	1300	5	10.19 ± 0.03	92.92 ± 0.31
4	120	1350	5	10.23 ± 0.02	93.21 ± 0.21
5	120	1250	5	10.07 ± 0.08	91.81 ± 0.74
6	60	1400	5	10.10 ± 0.03	92.05 ± 0.25
7	60	1050	5	9.92 ± 0.09	90.41 ± 0.81
8	60	1250	5	9.91 ± 0.12	90.38 ± 1.13
9	60	1450	5	10.15 ± 0.01	92.52 ± 0.11
10	100	1200	5	9.99 ± 0.02	91.10 ± 0.15
11	60	1500	5	10.08 ± 0.02	91.86 ± 0.18
12	60	1200	5	10.02 ± 0.05	91.34 ± 0.41
13	60	1300	5	10.04 ± 0.05	91.53 ± 0.43
14	60	1350	5	9.96 ± 0.07	90.79 ± 0.65
15	100	1200	1	10.11 ± 0.07	92.18 ± 0.62
16	100	1200	15	10.04 ± 0.07	91.51 ± 0.68
17	100	1300	1	10.18 ± 0.02	92.75 ± 0.18
18	100	1300	5	10.17 ± 0.01	92.69 ± 0.08
19	100	1300	15	10.12 ± 0.05	92.24 ± 0.48

Table 4: Bulk density and relative density of SPS-sintered UO_2 pellets (Part II).

Pellet ID	Pressure (MPa)	Temperature ($^{\circ}\text{C}$)	Time (min)	Density (g/cm^3)	TD (%)
20	100	1400	1	10.23 ± 0.12	93.24 ± 1.09
21	100	1400	5	10.17 ± 0.03	92.69 ± 0.27
22	100	1400	15	10.16 ± 0.08	92.60 ± 0.73
23	100	1500	1	10.15 ± 0.18	92.54 ± 1.63
24	100	1500	5	10.17 ± 0.02	92.70 ± 0.15
25	100	1500	15	10.30 ± 0.01	93.89 ± 0.13
26	120	1500	5	10.23 ± 0.01	93.21 ± 0.10
27	130	1300	5	10.17 ± 0.02	92.67 ± 0.20
28	100	1300	5	10.11 ± 0.02	92.12 ± 0.16
29	100	1300	5	10.16 ± 0.07	92.57 ± 0.61
30	100	1400	1	10.17 ± 0.04	92.68 ± 0.33
31	100	1400	1	10.14 ± 0.04	92.40 ± 0.38
32	140	1300	5	10.21 ± 0.02	93.03 ± 0.17
33	150	1300	5	10.21 ± 0.02	93.03 ± 0.21
34	160	1300	5	10.20 ± 0.05	92.99 ± 0.44
35	60	800	5	10.04 ± 0.01	91.55 ± 0.05

3.4. Punch displacement during SPS

Figure 3 shows the axial punch displacement as a function of time for SPS experiments conducted at a maximum temperature of 1300 °C and a holding time of 5 min, with applied pressures ranging from 60 to 160 MPa. In all cases, the displacement remains close to zero during the initial heating stage. A rapid increase in displacement is observed after passing the 800 °C point where the pressure is applied, followed by a gradual approach to a plateau. The end of the rapid displacement increase corresponds to the point at which the target pressure is reached. Lower pressures (60 and 100 MPa) result in limited displacement, whereas higher pressures (120–160 MPa) lead to significantly larger final displacement values. All experiments were performed using 2 g of powder per pellet, ensuring that the observed displacement variations reflect differences in SPS processing conditions rather than variations in sample mass.

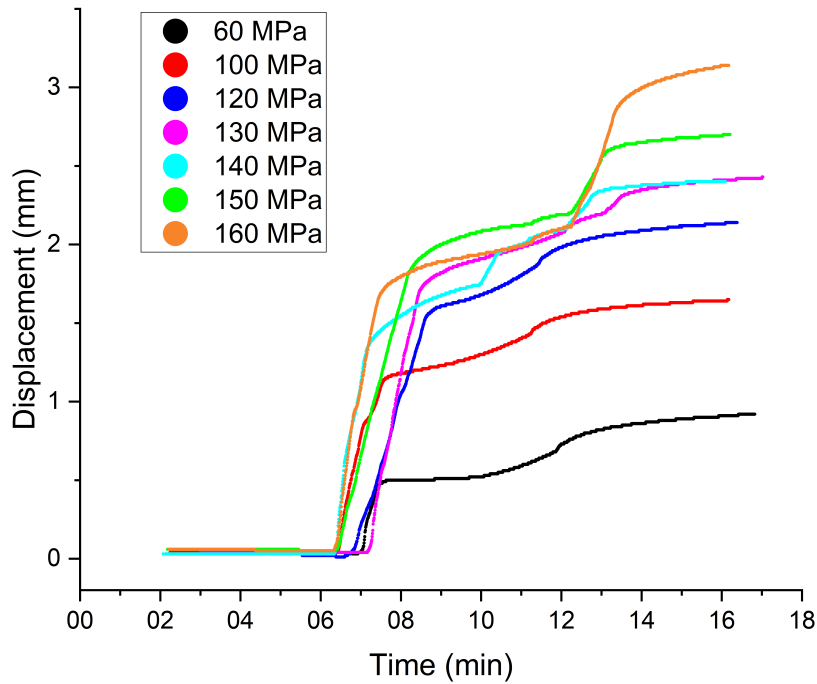


Figure 3: Axial punch displacement as a function of time during SPS at 1300 °C and 5 min holding time for different applied pressures. A rapid increase in displacement occurs upon pressure application at 800 °C, followed by a plateau, indicating transition from pressure-assisted compaction to diffusion-controlled densification. The recorded displacement includes contributions from both sample densification and the thermal and mechanical response of the graphite tooling and SPS assembly.

An additional increase in displacement is observed for the experiments conducted at 150 MPa and 160 MPa during the later stages of the SPS run. This behavior indicates minor deformation of the graphite tooling rather than additional densification of the pellet. The graphite die used in this study (Mersen grade 2333) has a reported compressive strength of approximately 167 MPa. Since the maximum applied pressure of 150–160 MPa approaches this mechanical limit, small elastic or plastic deformation of the tooling cannot be excluded. Such deformation would result in an apparent increase in punch displacement without a proportional change in pellet densification.

In the next Figure 4, the axial punch displacement as a function of time is presented. In this dataset, SPS experiments were carried out at a constant pressure of 100 MPa and a holding time of 5 min for maximum temperatures of 1200 °C, 1300 °C, 1400 °C, and 1500 °C. In all cases, the displacement remains close to zero during the early stages of the process, followed by a rapid increase at 800 °C as the pressure started to rise.

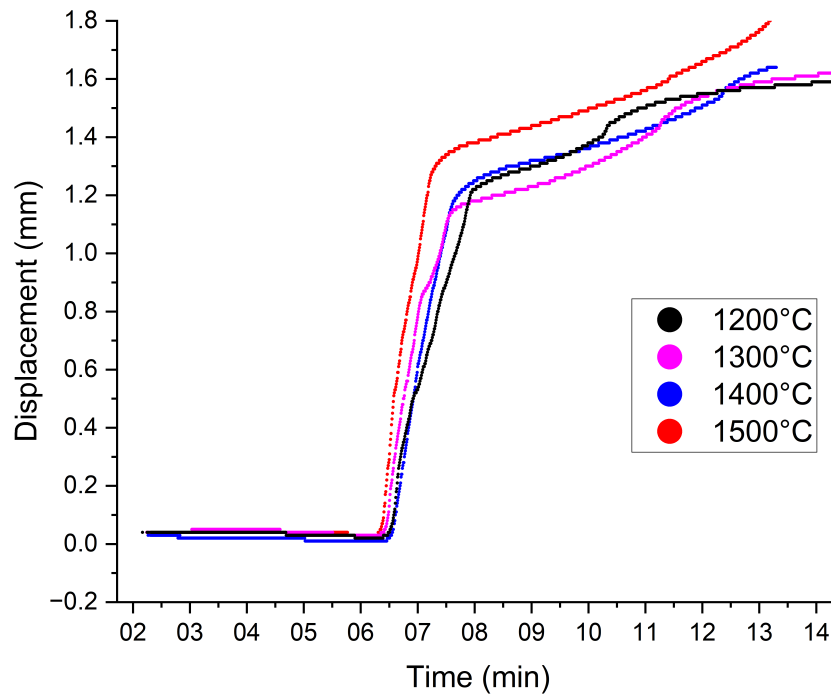


Figure 4: Axial punch displacement as a function of time during SPS at 100 MPa and 5 min holding time for different maximum temperatures. Higher temperatures lead to increased total displacement

3.5. Effect of Sintering Temperature on Relative Density

To evaluate the effect of sintering temperature on densification under fixed mechanical conditions, a series of UO_2 pellets was sintered at a constant applied pressure of 100 MPa and a holding time of 5 min, while varying the maximum sintering temperature. The resulting relative densities, determined by the Archimedes method, are presented as a function of temperature in Fig. 5.

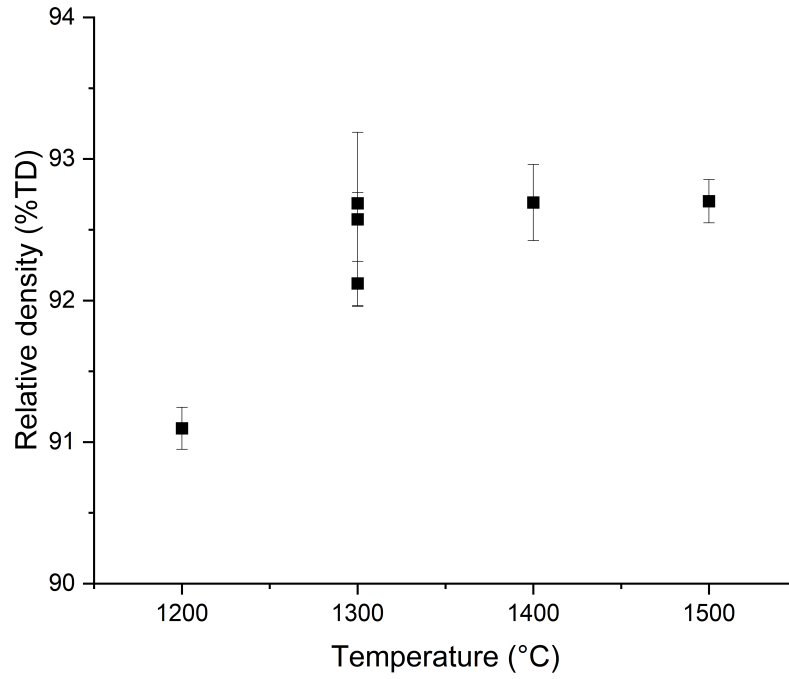


Figure 5: Relative density (%TD) as a function of temperature at 100 MPa and 5 min, showing limited densification above 1300 °C.

3.6. Effect of applied pressure on Relative Density

To isolate the influence of applied pressure on densification, an additional set of pellets was sintered at a constant temperature of 1300 °C and a holding time of 5 min, while varying the uniaxial pressure. The corresponding relative densities are plotted as a function of pressure in Fig. 6.

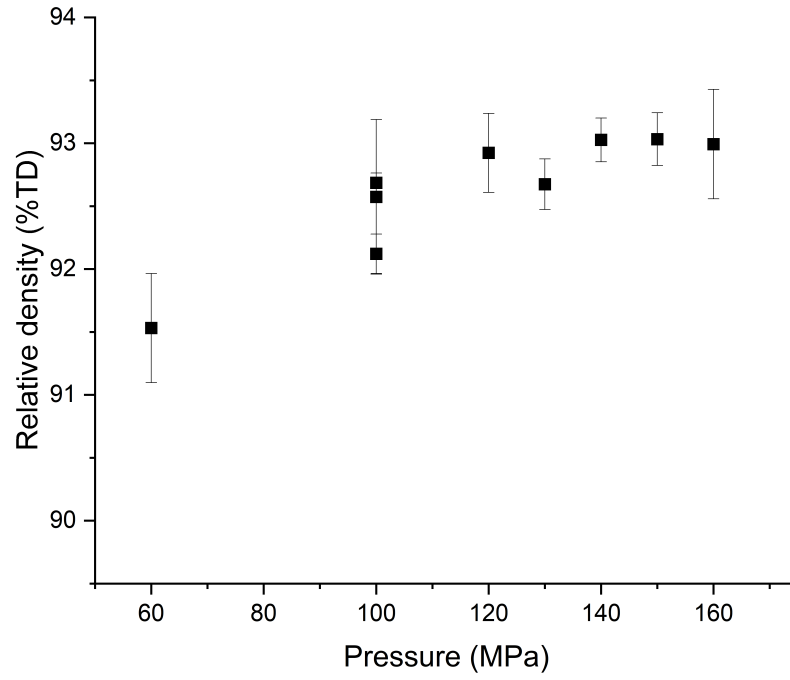


Figure 6: Relative density (%TD) as a function of pressure at 1300 °C and 5 min. Densification increases up to 100–120 MPa, with only minor changes at higher pressures.

3.7. Pressure–Temperature densification map

Based on the individual temperature- and pressure-dependent trends, a pressure–temperature map was constructed to provide an overview of the densification behavior of UO_2 under SPS conditions. The map summarizes the relative density achieved for pellets sintered at different combinations of temperature and pressure using a fixed holding time of 5 min, as shown in Fig. 7. Each marker represents an individual sintering condition, with the color scale indicating the achieved relative density.

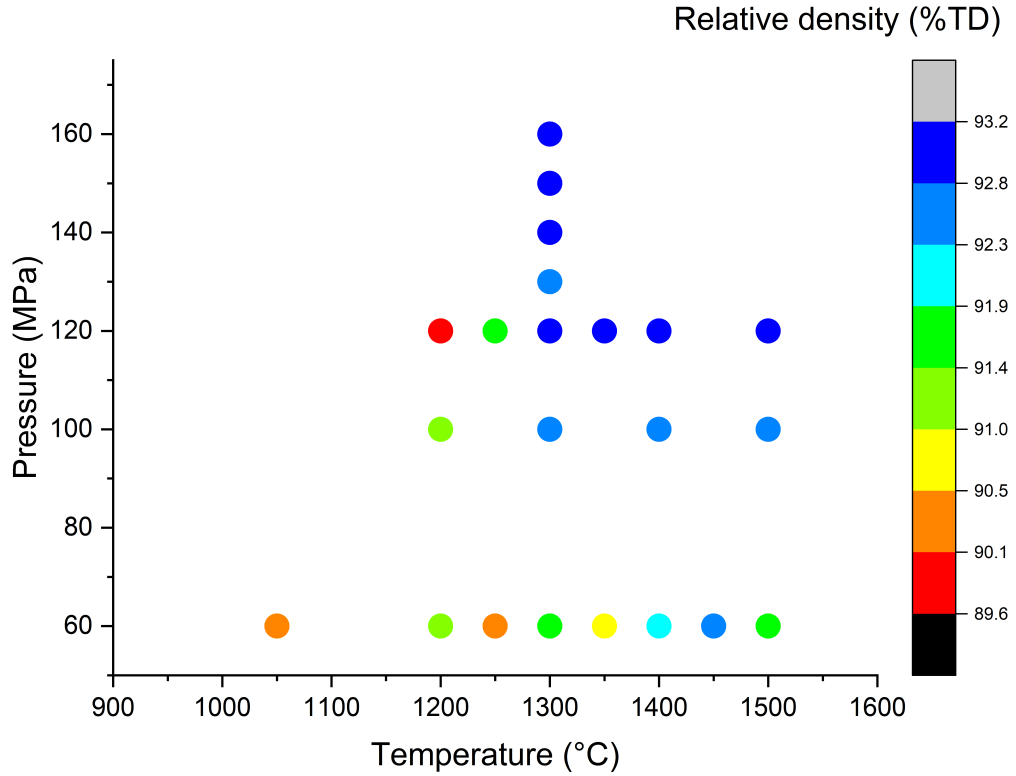


Figure 7: Pressure–temperature map of relative density (%TD) for UO_2 pellets sintered with a constant holding time of 5 min. The map indicates a densification plateau above 1300 °C and 100–120 MPa, defining an upper density limit of approximately 93–94% TD for the investigated powder.

3.8. Quantitative porosity analysis by ImageJ

To complement the bulk density measurements, a subset of pellets processed under representative SPS conditions was selected for quantitative porosity analysis. Porosity was evaluated from SEM images using ImageJ image analysis, and the resulting values are summarized in Table 5.

Table 5: Porosity determined by ImageJ analysis for selected UO_2 pellets sintered under representative SPS conditions.

Pellet ID	Sintering conditions	Porosity (%)
10	100 MPa – 1200°C – 5 min	21.8
18	100 MPa – 1300°C – 5 min	5.6
24	100 MPa – 1500°C – 5 min	4.8
34	160 MPa – 1300°C – 5 min	4.4

Representative SEM micrographs of the analyzed pellets are presented in Fig. 8. These images illustrate the evolution of the microstructure and the distribution of residual pores under different SPS processing conditions.

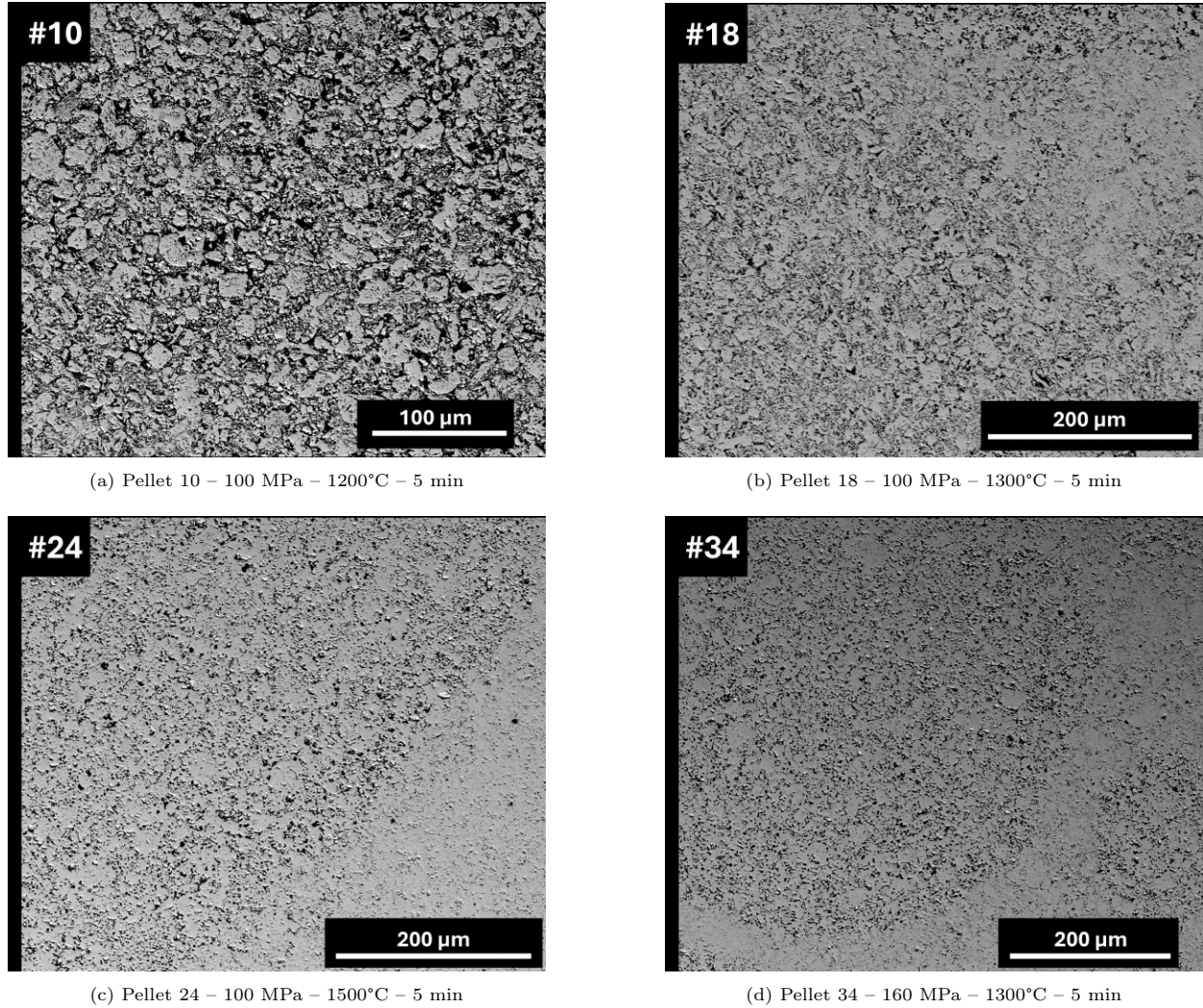


Figure 8: SEM micrographs of selected UO_2 pellets illustrating the evolution of microstructure with SPS conditions. Increasing temperature and pressure reduce porosity, but residual pores remain visible.

3.9. Correlation between punch displacement and Relative Density

The final displacement recorded during Spark Plasma Sintering is plotted as a function of the relative density for pellets sintered with a constant holding time of 5 min (Fig. 9). Restricting the dataset to a fixed holding time allows the relationship between axial shrinkage and final densification to be examined independently of time effects. The data include pellets processed over all the range of sintering temperatures and applied pressures, while the dashed line is included solely as a guide to the eye.

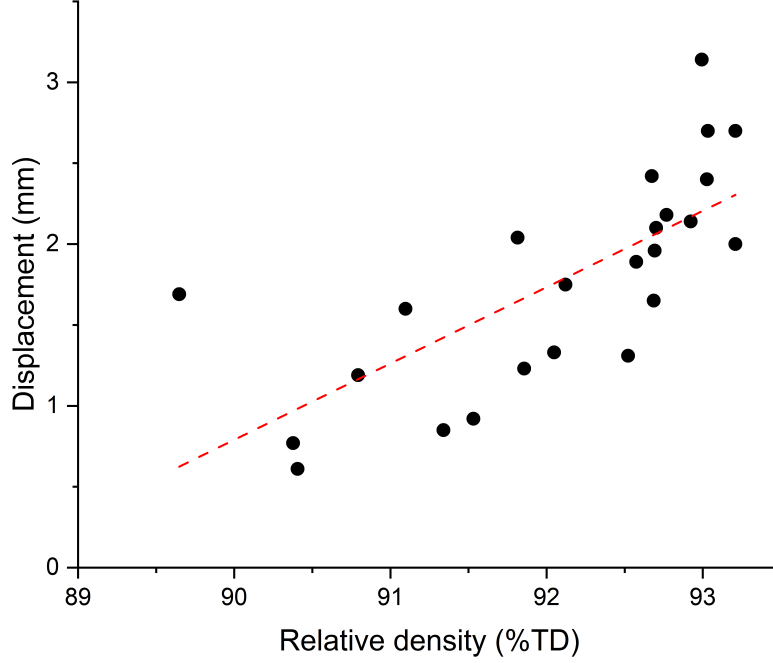


Figure 9: Final axial displacement as a function of relative density for pellets sintered with a holding time of 5 min. A positive correlation is observed. Deviations at high displacement values indicate contributions from tooling deformation rather than effective densification.

4. Discussion

The relative densities obtained after SPS range between approximately 89% and 94% of theoretical density, indicating moderate but not full densification under the investigated conditions. Although SPS is generally capable of achieving near-theoretical densities in UO_2 , the densification behavior is strongly dependent on the characteristics of the starting powder.

The initial UO_2 powder exhibits a low specific surface area of $0.27 \text{ m}^2\text{g}^{-1}$ and a mean particle size of $1.8 \text{ }\mu\text{m}$, as confirmed by SEM. Such low surface area particles provide a relatively small surface energy driving force for sintering compared to powders with higher specific surface area. Consequently, particle rearrangement and neck growth during SPS are less efficient, limiting the achievable densification even under high pressure and rapid heating conditions[13].

Although the observed densification limit is consistently associated with the low specific surface area of the starting powder, the present study does not include a direct experimental comparison with higher surface area UO_2 powders. Therefore, the role of surface area is inferred based on established sintering theory and comparison with literature data, where higher surface area powders typically achieve near-theoretical densities under similar SPS conditions [5, 6, 7, 8, 9, 10]. The present results should thus be interpreted as strong evidence that the intrinsic powder characteristics dominate densification behavior in this case, rather than as an isolated proof of causality.

The moderate relative densities observed in this study are therefore consistent with the relatively coarse, low-surface-area nature of the starting powder rather than with insufficient SPS parameters. Increasing the surface area, for example by choosing a different powder synthesis route, would be expected to enhance densification and promote the achievement of higher theoretical density values.

The limited densification cannot be attributed to oxygen non-stoichiometry, as XRD analysis confirmed a composition of $\text{UO}_{2.00\pm0.01}$. At this level of deviation, defect concentrations remain within the typical range for stoichiometric UO_2 and are not expected to significantly alter sintering kinetics.

Despite the substantial increase in displacement at higher pressures, the final relative densities remain below full theoretical density. This indicates that while pressure enhances particle rearrangement and contact formation, the overall densification is ultimately limited by the coarse particles and low specific surface area of the starting powder, which reduce the diffusion driving force during the sintering process.

The punch displacement curves reveal a two-stage densification process. During initial heating, displacement remains negligible. At approximately 800 °C, the manually applied pressure induces a sharp increase in displacement, corresponding to rapid particle rearrangement and pressure-assisted plastic deformation. Minor deviations between curves in this region are attributed to small variations in the manual pressure ramp. Following this rapid compaction stage, the displacement rate decreases and progressively approaches a plateau. This second stage is governed by thermally activated diffusion mechanisms responsible for neck growth and pore shrinkage[13]. The transition from mechanically dominated to diffusion-controlled densification is clearly visible in all experiments.

At constant pressure (100 MPa) and holding time (5 min), increasing the temperature from 1200 °C to 1300 °C produces a noticeable increase in relative density. However, further temperature increases to 1400 °C and 1500 °C yield only marginal additional densification. While total displacement continues to increase with temperature, the relative density stabilizes around 93% TD. This behavior indicates that beyond approximately 1300–1400 °C, densification becomes limited by pore isolation and diffusion kinetics. Once pores become closed or trapped within grains, further temperature increases contribute less efficiently to density improvement.

At constant temperature (1300 °C) and holding time (5 min), increasing the applied pressure from 60 to 100 MPa leads to a clear improvement in both displacement and relative density. However, further increases up to 160 MPa result in only modest gains in density despite significantly higher displacement values. This suggests that pressure strongly enhances particle rearrangement and early-stage compaction but has a reduced impact once diffusion-controlled mechanisms dominate. Above approximately 100–120 MPa, densification becomes less sensitive to pressure, indicating that the controlling mechanism is no longer purely mechanical.

Within the investigated dwell time range (1–15 min), no systematic increase in relative density was observed at constant temperature and pressure. Most densification occurs during heating and immediately after pressure application, while the subsequent isothermal holding stage contributes only marginally to further pore elimination. This further supports the interpretation that densification rapidly reaches a diffusion-limited regime under the present conditions.

The pressure–temperature map of relative density at 5 min holding time illustrates a clear densification domain. Higher densities are achieved at intermediate-to-high pressures (100–160 MPa) and temperatures above 1300 °C; however, a plateau is evident, confirming the presence of an upper densification limit under the current powder characteristics.

The correlation between punch displacement and relative density shows a positive trend, indicating that axial shrinkage provides a reliable qualitative indicator of densification progress. Nevertheless, the relationship is not strictly linear. At higher pressures and temperatures, displacement continues to increase while density gains diminish. This decoupling suggests that part of the additional shrinkage is associated with tooling deformation rather than effective pore elimination.

A direct comparison with previously reported SPS studies must take into account the differences in the characteristics of the starting powders. In other publications, the UO_2 powders used for SPS exhibit much larger apparent particle sizes, typically ranging from 5–50 μm or even 5–60 μm , with mean particle sizes around 30 μm [7, 9]. However, these coarse particles often correspond to agglomerates composed of much finer primary grains, which can result in relatively high specific surface areas and enhanced sintering activity.

In contrast, the powder used in the present study consists of relatively dense micrometer-sized particles with a mean size of about 1.8 μm and a very low specific surface area ($0.27 \text{ m}^2\text{g}^{-1}$). As a consequence, the driving force for sintering is reduced, which contributes to the lower densification levels observed in the present SPS experiments compared to values reported in the literature under otherwise similar temperature and pressure conditions.

The SEM micrographs presented in Fig. 8 illustrate the microstructural state of pellets sintered under different SPS conditions. Pellet 10 (1200 $^{\circ}\text{C}$, 100 MPa) clearly appears undersintered, with a highly porous microstructure and poorly consolidated particle network, consistent with the lower relative density measured for this condition. In contrast, pellets 18, 24, and 34 exhibit significantly more compact microstructures, with a more homogeneous distribution of smaller pores. However, no major qualitative differences can be observed between these three samples despite the variations in temperature and pressure. In all cases, individual grains are not distinguishable in the SEM images, suggesting that the microstructure remains dominated by partially consolidated particles rather than well-developed sintered grains. These observations are consistent with the relatively moderate densification levels obtained and indicate that the applied SPS conditions were sufficient to promote particle bonding but not to produce a fully developed grain structure.

Overall, the combined analysis of displacement curves, density evolution, holding time experiments, and the SPS map demonstrates that densification in the present study is initially pressure-assisted but ultimately limited by diffusion kinetics associated with the coarse particles, low-surface-area starting UO_2 powder. The intrinsic powder characteristics therefore represent the dominant factor controlling the attainable density within the investigated SPS parameter space.

5. Conclusions

A systematic SPS parameter map of low surface area UO_2 powder was established by varying temperature (800–1500 $^{\circ}\text{C}$), pressure (60–160 MPa), and holding time (1–15 min). The results show that densification increases with both temperature and pressure; however, the achievable relative density remains limited to approximately 93–94% TD under the investigated conditions. Punch displacement curves reveal a two-stage densification process consisting of rapid pressure-assisted particle rearrangement followed by diffusion-controlled pore elimination. Most densification occurs during heating and immediately after pressure application, while extending the holding time provides only marginal additional improvement.

The densification plateau observed at high temperature and pressure is attributed primarily to the characteristics of the starting powder, which exhibits a low specific surface area ($0.27 \text{ m}^2\text{g}^{-1}$) and mean particle size of 1.8 μm . The near-stoichiometric composition ($\text{UO}_{2.00\pm0.01}$) indicates that oxygen non-stoichiometry is minimal and therefore unlikely to significantly influence the sintering behavior. Overall, the SPS map demonstrates that, for the present powder, densification is initially pressure-assisted but ultimately controlled by intrinsic powder characteristics, resulting in an upper density limit of approximately 93–94% TD within the explored processing window.

6. Acknowledgements

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