

**SPACE NUCLEAR POWER SYSTEMS:
ENABLING INNOVATIVE SPACE
SCIENCE
& EXPLORATION MISSIONS**

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SPACE NUCLEAR POWER SYSTEMS: ENABLING INNOVATIVE SPACE SCIENCE & EXPLORATION MISSIONS

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Abstract

The European Space Agency's (ESA's) ^{241}Am radioisotope power systems (RPSs) research and development programme is ongoing. The chemical form of the americium oxide 'fuel' has yet to be decided. The fuel powder will need to be sintered. The size and shape of the oxide powder particles are expected to influence sintering. The current chemical flow-sheet creates lath-shaped AmO_2 . Investigations with surrogates help to minimise the work with radioactive americium.

This study has proposed that certain cubic $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ oxides (Ia-3 crystal structures with $0.5 < x < 0.7$) could be potential surrogates for some cubic $\text{AmO}_{2-(x/2)}$ phases. A new wet-chemical-synthesis-based process for fabricating $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a targeted x -values has been demonstrated. It uses a continuous oxalate coprecipitation and calcination route. An x of 0.6 was nominally targeted. Powder X-ray diffraction (PXRD) and Raman spectroscopy confirmed its Ia-3 structure. An increase in precipitation temperature (25 °C to 60 °C) caused an increase in oxalate particle median size. Lath/plate-shaped particles were precipitated. Ce Nd oxide PXRD data was Rietveld refined to precisely determine its lattice parameter. The data will be essential for future sintering trials with the oxide where variations in its crystal structure during sintering will be investigated.

Sintering investigations with micrometric CeO_2 and Nd_2O_3 have been conducted to understand how AmO_2 and Am_2O_3 may sinter. This is the first reported pure Nd_2O_3 spark plasma sintering (SPS) investigation. A comparative study on the SPS and the cold-press-and-sinter of CeO_2 has been conducted. This is the first study to report sintering lath-shaped CeO_2 particles. Differences in their sizes and specific surface areas affected powder cold-pressing and caused variations in cold-pressed-and-sintered CeO_2 relative density and Vickers hardness. The targeted density range (85-90%) was met using both sintering techniques. The cold-press-and-sinter method created intact CeO_2 discs with reproducible geometry and superior Vickers hardness to those made by SPS.

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tea,

and with this, I quote:

“ ‘It began with the tea’, the Hatter replied.”

— Lewis Carroll, Alice’s Adventures in Wonderland,

and so with this, I begin...

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¹ The image reuse permission has required the caption of the original image to be stated. This is the reason for the American spelling of fibre.

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LIST OF ACRONYMS

ASRG	Advanced Stirling Generator
BSE	Back scattered electrons
DOE	Department of Energy
ESA	European Space Agency
ESEM	Environmental scanning electron microscope
GoF	Goodness of fit
GPHS	General Purpose Heat Source
IPF	Instrumental profile function
LWRHU	Light Weight Radioisotope Heater Unit
MMRTG	Multi-Mission Radioisotope Thermoelectric Generator
NASA	National Aeronautics and Space Administration
NIST	National Institute of Standards and Technology
NNL	National Nuclear Laboratory
NPL	National Physical Laboratory
PDF	Powder diffraction file
PIDS	Polarised Intensity Differential Scattering
PXRD	Powder X-ray diffraction
QXRF	Quantitative X-ray fluorescence
REO	Rare earth oxide
RHU	Radioisotope heater unit

RMS	Root mean square
RPM	Revolutions per minute
RPS	Radioisotope power system
RTG	Radioisotope thermoelectric generator
SE	Secondary electrons
SEM	Scanning electron microscope
SNAP	Systems for Nuclear Auxiliary Power
SPS	Spark plasma sintering
SRM	Standard reference material
T.D.	Theoretical density
TGA	Thermogravimetric analysis
U.S.	United States
UDRI	University of Dayton Research Institute
UoL	University of Leicester
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER 1: INTRODUCTION

1. Radioisotope Power Systems: Key Enabling Technologies

Radioisotope Power Systems (RPS) enable exploration of some of the more challenging environments in the solar system such as deep space and planetary surfaces. These power systems are independent of the local solar intensity in contrast to solar array power systems. In general, spacecraft exploring these distant regions from the Sun e.g. as far as Jupiter and beyond, would require solar arrays that would be prohibitively large in order to meet their electrical power requirements. However, the advanced solar array technologies that have been developed in recent years have enabled space missions to Jupiter and Comet 67P, namely, the National Aeronautics and Space Administration's (NASA) Juno mission and the European Space Agency's (ESA) Rosetta mission, respectively (Kayali et al., 2012, ESA). Nonetheless, exploring space at these distances from the Sun with solar power systems can restrict the choice and design of a spacecraft's trajectory and constrain the mission as a whole. For example, the Juno spacecraft was designed to have a Sun-facing science orbit (NASA, 2016a). This helped to minimise the solar array area required to meet the spacecraft's power needs. An advantage, therefore, of using RPSs in these more extreme environments is that it allows flexibility in the choice of a science orbit's trajectory and therefore, in theory, could enable a wider range of science questions to be addressed.

Radioisotope power systems also offer longevity and can enable science missions to return data for several years beyond the nominal mission duration. For example, the Voyager 1 and 2 spacecrafts that are electrically powered by multi-hundred Watt (MHW) RTGs were launched in 1977 and the power systems are predicted to function until 2025 (Idaho National Laboratory Batelle Energy Alliance, 2015, U.S. Department of Energy, 2017). Voyager 1 was the "first man-made object to enter interstellar space" (U.S. Department of Energy, 2017, NASA and JPL-Caltech, 2013).

1.1. Radioisotope Heater Units (RHUs)

RHUs are a type of RPS. They are ideal for missions where the electrically powered heater would use a large fraction of a spacecraft's power budget, and therefore impact the number and choice of the science instruments for a given science mission. Therefore using RHUs could have a positive influence on the power and mass budget of a spacecraft

with respect to the science instruments. RHUs can be easily placed at their required locations owing to their small size (Idaho National Laboratory Batelle Energy Alliance, 2015). The light-weight radioisotope heater unit (LWRHU) developed by the U.S. Department of Energy (DOE) is illustrated in Figure 1.1. Each generates around 1 Watt of thermal power; is ~40 g in mass; ~3.2 cm in height and 2.6 cm in diameter (NASA, 2016b).

Two iconic examples of the use of RHUs were the first Apollo mission and the Cassini-Huygens mission. In the former, two RHUs kept the Early Apollo Scientific Experiment Package warm during the lunar nights, which were 14 Earth days each (Idaho National Laboratory Batelle Energy Alliance, 2015). The Cassini-Huygens mission used 117 LWRHUs, which have a more modern design.



Figure 1.1: Illustrates a U.S. LWRHU (NASA, 2016b). Image Credit: U.S. Department of Energy.

1.2. Radioisotope Thermoelectric Generators (RTGs) and Stirling Generators

RTGs and Stirling generators are types of RPS that convert decay heat from a radioisotope into electricity. An RTG utilises the Seebeck effect of thermoelectric materials: when a temperature differential is applied across a thermoelectric material, a current is generated. The design of thermoelectric materials is an ongoing research area in the space nuclear power field. Stirling generators use Stirling engine technology. The advantage of this technology over RTGs is its potential to provide a higher conversion efficiency and higher specific electrical power (Glossary). Examples of such statistics for the Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) system and the Advanced Stirling Generator (ASRG) are provided in Table 1.1. The heritage of RTGs and the challenges associated with Stirling generator development have made RTGs the preferred option for

NASA missions. The discontinuation of ASRG procurement was announced in 2013 (Green, 2013).

*Table 1.1: Statistics on the MMRTG and ASRG radioisotope power systems. *Beginning of mission. †Beginning of life.*

RPS	Conversion Efficiency (%)	Specific Electrical Power ($W_e \text{ kg}^{-1}$)	Reference
MMRTG	6	2.8 *	(NASA,2014)
ASRG	29 [†]	4.9 [†]	(Chan et al., 2014)

RPSs have heritage dating back to the 1960s. The first spacecraft to use an RPS in space was the Transit 4A, which used a *Systems for Nuclear Auxiliary Power* (SNAP) program RPS (Idaho National Laboratory Batelle Energy Alliance, 2015). The versatility of RPSs has enabled several missions including many of the Apollo lunar landings (see Figure 1.2) and NASA’s Mars Science Laboratory that has its *Curiosity* rover powered by an MMRTG (Idaho National Laboratory Batelle Energy Alliance, 2015). Figure 1.3a is a pull-apart image of the MMRTG that illustrates several of its components including the thermoelectric modules that convert the heat into electricity and the modular heat sources known as General Purpose Heat Sources (GPHS). The General Purpose Heat Source RTGs that were flown on Cassini, and more modern U.S. RTGs comprise these heat sources. GPHSs are stacked in an MMRTG system. Each GPHS module contains $^{238}\text{PuO}_2$ pellets surrounded by multiple containment layers (including cladding, impact and ablative layers; see Figure 1.3b) that provide protection against environmental exposure in potential launch accident and Earth re-entry scenarios. An RPS is thus not only designed for its specific power performance (see Glossary) but also with inherent safety features built in. These features are designed throughout the system. For example, PuO_2 is a high temperature ceramic material (Schmidt et al., 2011). High temperature ceramic fuel pellets are able to withstand extremely high temperatures e.g. in high temperature accident scenarios. The radioactive material is typically referred to as the ‘fuel’.

It is important to emphasise that other countries have developed and used RPSs for space. For example, Russia has developed the Angel RHU and Angel RTG that each use $^{238}\text{PuO}_2$

as the fuel that produce² 0.2 W_e and 8.5 W_t , respectively (Pustovalov, 2007). The reader is referred to Pustalov (2007) for further details.

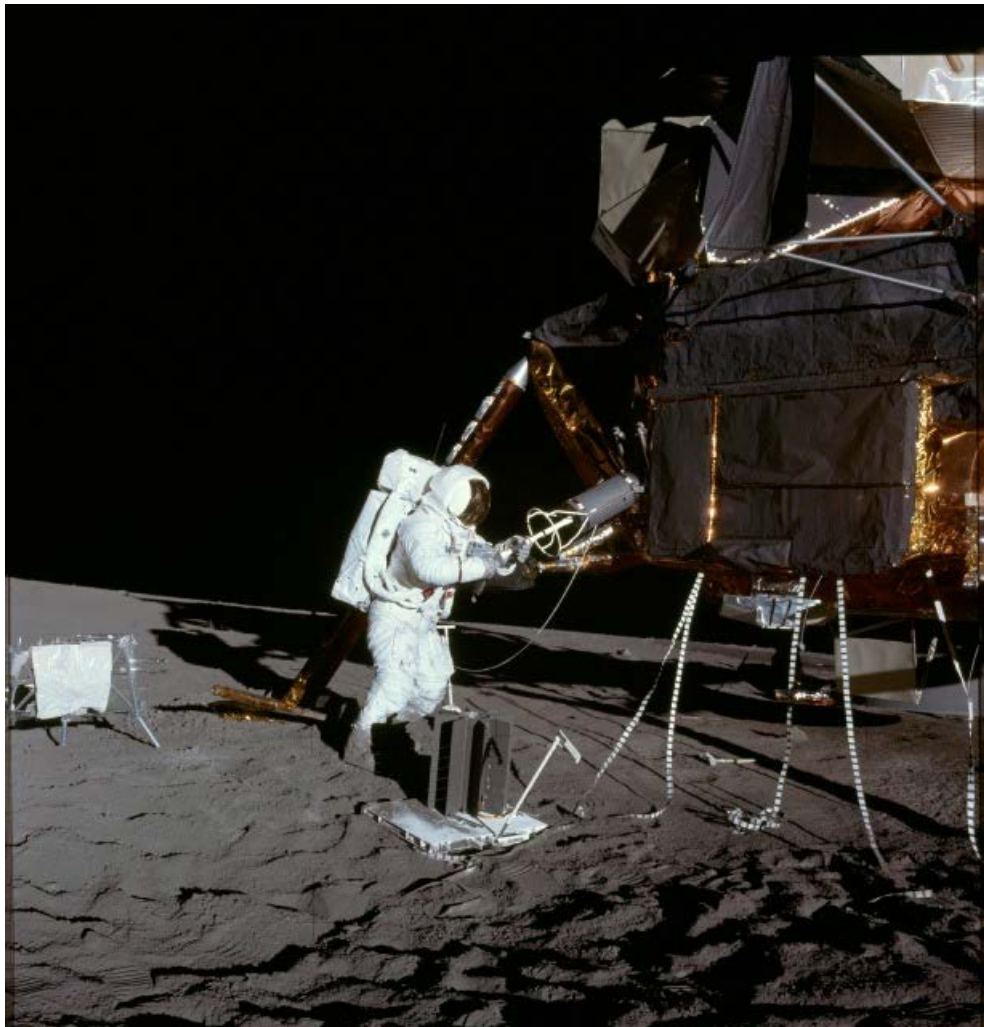


Figure 1.2: illustrates “Apollo 12 mission with astronaut Alan Bean removing the SNAP-27 heat source from its carrying cask to insert it into the RTG housing.” Explanation provided by Idaho National Laboratory Batelle Energy Alliance (2015). Image courtesy of spaceflight.nasa.gov.

² W_e and W_t are used to denote ‘Watts of electrical power’ and ‘Watts of thermal power’, respectively. This is common notation.

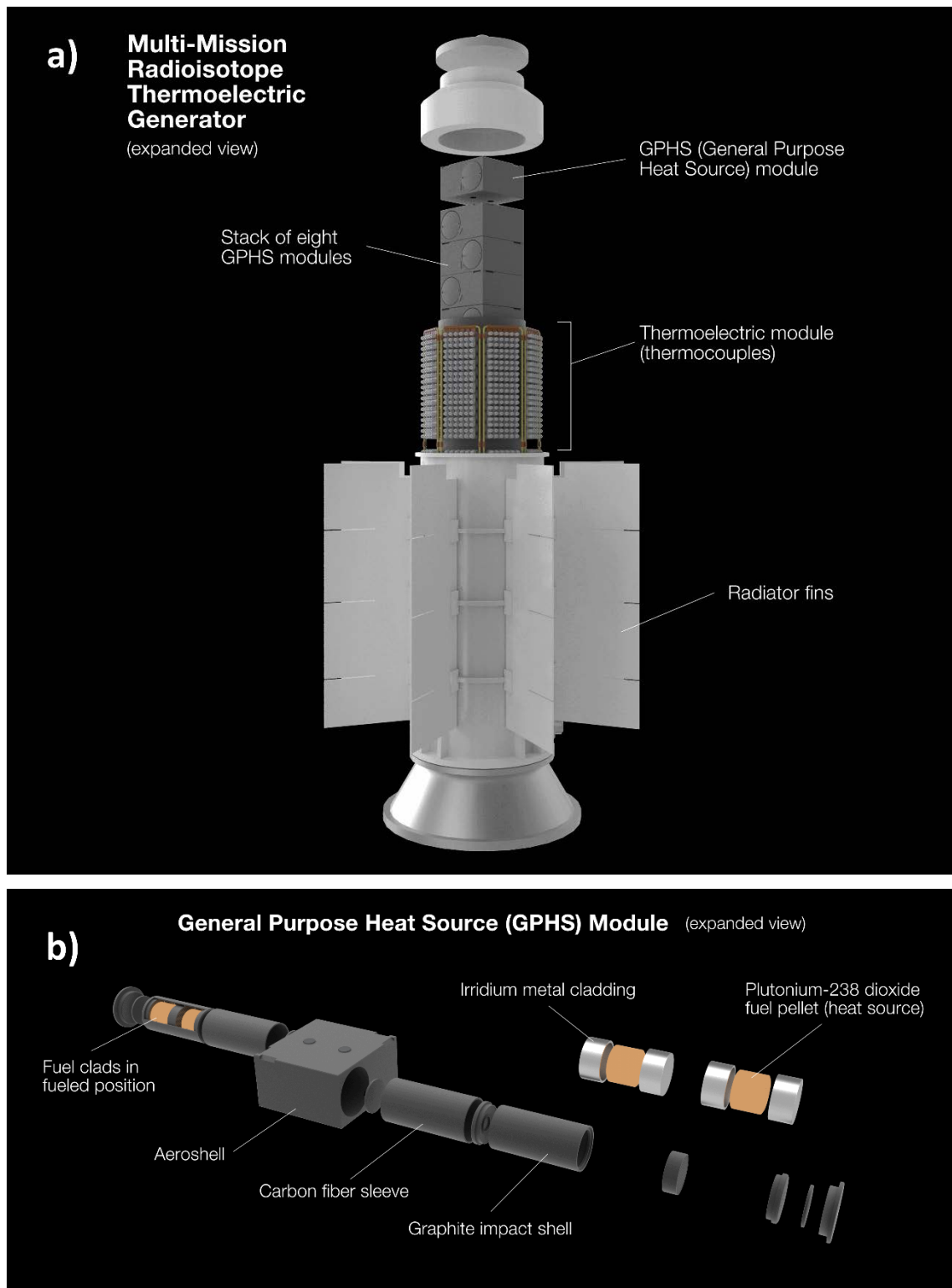


Figure 1.3: Pull-apart images of the a) Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) and b) a General Purpose Heat Source (GPHS) Module. Image courtesy of NASA.

2. The ESA RPS Programme

Since the U.S. production of ^{238}Pu was halted in the late 1980s, the dwindling stock available for NASA science missions has threatened to limit the number of RPS-powered missions (National Research Council, 2009). A planned re-start of production will be on a small scale and ^{238}Pu will remain a very scarce resource for the foreseeable future (Wham et al., 2015).

In 2008, the European Space Agency (ESA) began a research and development programme into the production of a European RPS (Summerer et al., 2012, Ambrosi et al., 2012, Williams et al., 2012, Williams et al., 2013). Americium-241 (^{241}Am) was selected as the RPS fuel choice. It was identified as a potentially viable, and affordable, alternative for Europe (Summerer et al., 2012) despite its lower specific thermal power than ^{238}Pu (Summerer et al., 2012, O'Brien et al., 2008). Research into americium oxide production and processing as well as into the development of different RPS technologies is being pursued in the programme. Such technologies include RTGs (Ambrosi et al., 2012), Stirling Generators (Summerer et al., 2012), and Radioisotope Heater Units (RHUs). The University of Leicester (UK) is leading several research and development (R&D) activities, which include but are not limited to:

- 10 W_e RTG development
- Modular heat source development
- RHU design, which includes its encapsulation e.g. cladding and insulation layers.

The National Nuclear Laboratory (UK) is leading the fuel R&D activities. NNL has developed a chemical processing method for extracting ^{241}Am from ^{241}Pu civil reserves in the UK and have demonstrated that it can be transformed into an Am oxide powder via an oxalate precipitation and calcination route (see Chapter 2 for an explanation of these processes). This research is still under development.

2.1. Early Requirements of the Fuel

The americium oxide fuel will need to be in a form that can be integrated easily into an RPS system. This will require the americium oxide powder to be consolidated into structures such as pellets or discs that have handling strength and that can be incorporated into clads (see Figure 1.4). This will then form part of a modular heat source. The ability to sinter (see Glossary) americium oxides into pellets or discs with, for

example, high relative density as well as mechanical and chemical stability, is an essential part of the ESA-funded programme. Oxide powder particle characteristics such as size and morphology could influence how the material sinters and therefore the resultant pellet properties such as density. A good understanding of the chemical and physical properties of the raw oxide material, its sinterability and the mechanical properties of the sintered product will need to be established. This will be necessary for the development of a safety framework for European radioisotope power systems. Consolidating the powder into a pellet will also provide an inherent safety design feature that will help to guard against respirable fine dispersal should the final pellet containment layer, i.e. the cladding, be breached in a launch accident scenario.

Some of the early generated requirements for a sintered fuel body e.g. a pellet, for RTGs or RHUs are to:

1. Create an intact sintered body with a reproducible geometry.
2. Create sintered bodies that will each have a relative density (see Glossary) that will allow for He from the α -decay of the ^{241}Am to outgas through the pellet and to be vented through the cladding structure. For example, a density of around 85-90 % of theoretical density (T.D.) would be suitable. The objective is to avoid pellet swelling that could adversely affect the cladding integrity and impact safety.
3. Create RHU sintered bodies that will each provide $3 W_t$ and to create RTG sintered bodies that will each provide $66.6 W_t$ at beginning of life, respectively.
4. Create sintered bodies with crystal structures and oxygen-to-metal ratios that remain stable at their operating temperatures over extended times.
5. Not chemically react with the cladding material in a way that could change the thermal properties of the fuel and clad and therefore affect heat transfer.
6. Not chemically react with the cladding material in a way that could change the mechanical properties and structural integrity of the clad.
7. Contain minimal impurities including carbon from the oxalate precipitation process that could react with the fuel form or the clad material.

Requirement number 3 will in turn require a reproducible manufacturing process, which will include using a reproducible americium oxide fuel form in terms of its chemistry (oxygen to metal ratio); crystal structure; particle characteristics such as shape and size, specific thermal power prior to its sintering and a reproducible sintering process.

The thermal conductivity is an important property of the americium oxide fuel for consideration for RPS designs. However, there are no RPS design requirements for its value. This is because the thermal conductivities of the different chemical forms of americium oxides are similar and range between around 0.7 and 1.75 W m⁻¹ K⁻¹ at temperatures above 800 K (Lemehov et al., 2003).

The specific activity of pure ²³⁸Pu is approximately five times greater than that of pure ²⁴¹Am at 17.13 Ci g⁻¹ and 3.43 Ci g⁻¹, respectively (O'Brien, 2010). However, the current design for an AmO₂ RHU pellet that would generate ~3 W_t (see Chapter 6) would have an activity that is around 3 times that of the U.S. 1 W_t LWRHU. It is therefore essential that the designs of the ESA sintered fuel bodies will need to address helium production.

Requirement number 3 states that any produced helium will need to be outgassed through the pellet to avoid pellet swelling. The U.S. GPHS and LWRHU systems are designed to allow helium generated in the ²³⁸PuO₂ pellets to outgas (Peterson, 1984). A literature review by El-Genk et al. (2000) states that the helium release fractions of the GPHS and RHU ²³⁸PuO₂ pellets are related to the grain size. Small grain sizes allow helium release more readily than larger grain sizes (McDonnell, 1978, Peterson, 1984). The former also allow helium transport to the pellet surface, which results in less trapped helium in the grain boundaries (Peterson, 1984). The aforementioned ²³⁸Pu literature suggests that the design of the microstructure and porosity will be key to controlling He outgassing.

The requirements for the microstructures and porosities of the ESA RPS and RHU sintered bodies have not yet been established at this early stage of the programme. There have also been no known published studies on the effect of helium outgassing of americium oxide pellet microstructure. This will be a key aspect of the future fuel research and development. As stated in requirement number 3, swelling will need to be avoided. This is to ensure cladding integrity and performance is unaffected during accident scenarios e.g. launch pad fire or Earth re-entry.

Requirements 1 and 2 are the focus of this thesis.

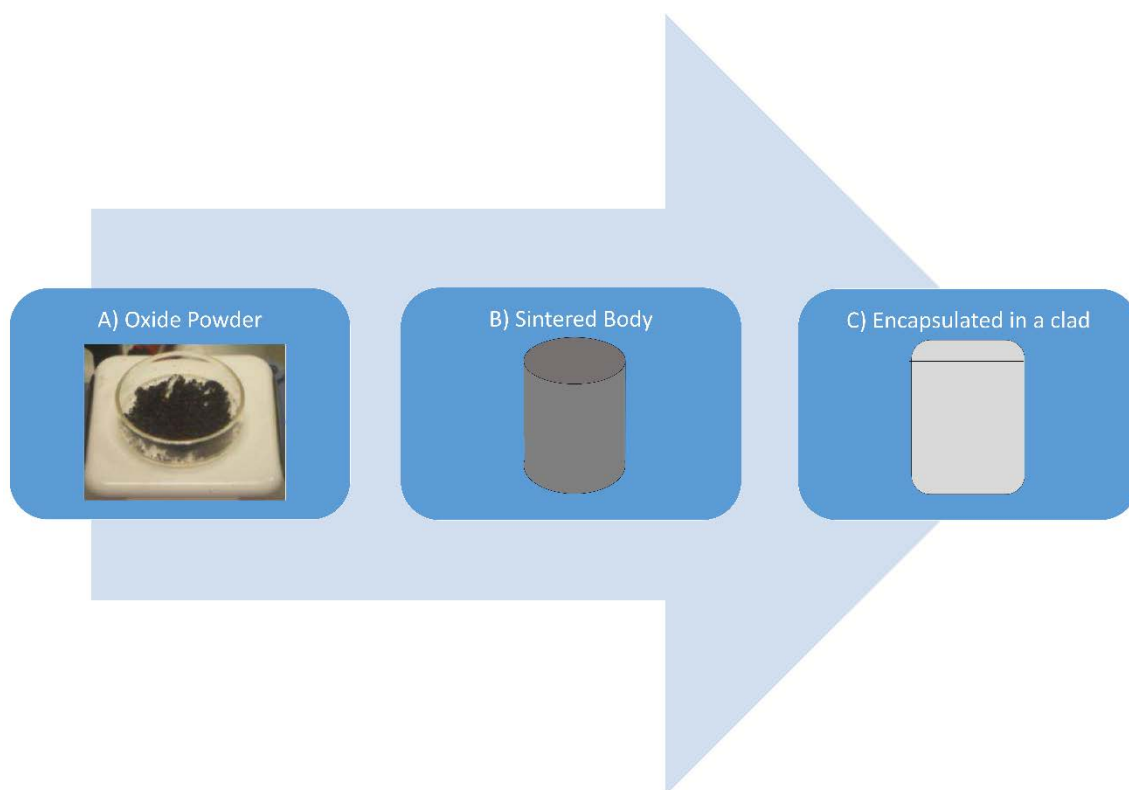


Figure 1.4: A schematic illustrating how a powder will need to be sintered into a form that can be incorporated into a clad. Not to scale. For example purposes only, a photograph of AmO_2 powder generated by the current ESA chemical flow sheet (see § 3 of Chapter 2) is shown (Sarsfield, 2016a).

2.2. Americium Oxide Choice

Research into different forms of americium oxide is ongoing to decide which chemical form of the fuel should be used. There are a number of feasible solid oxides ranging from americium sesquioxide (Am_2O_3), which has an oxygen-to-metal ratio of 1.5, through to americium dioxide (AmO_2), which has an oxygen-to-metal ratio of 2.0. This is illustrated in the americium-oxygen phase diagram shown in Figure 1.5. The intermediary phases are typically described as AmO_{2-x} phases where x ranges from 0.5 to 0. Alternatively, these phases can be described as $\text{AmO}_{2-(x/2)}$ phases where x ranges between 0 and 1. This notation is used throughout this thesis.

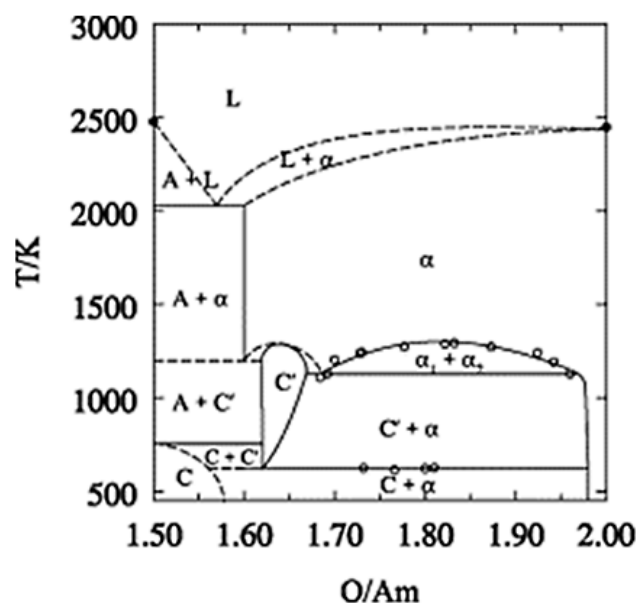


Figure 1.5: The tentative Am-O phase diagram³ by Thiriet and Konings (2003), which also illustrates data (circles) measured by Sari et al. (1970). The C phase corresponds to cubic (Ia-3) Am_2O_3 ; the A phase to hexagonal Am_2O_3 ; the C' phase to a higher temperature cubic (Ia-3) phase and all α phases to face centred cubic $\text{AmO}_{2-(x/2)}$.

2.3. Early Fuel Development Objectives

A wide range of experiments will be required to establish how the initial requirements outlined in § 2.1 can be achieved. Investigations with suitable surrogate materials are valuable to minimise the number of experiments with highly radioactive americium. In this context, a surrogate is a non-radioactive material that has some similar characteristics to a radioactive material of interest e.g. crystal structure and particle morphology. Cerium(IV) oxide (CeO_2) and neodymium(III) oxide (Nd_2O_3) are used as surrogates for americium dioxide (AmO_2) and americium sesquioxide (Am_2O_3), respectively. The rationale for their use is outlined in Chapter 5 of this thesis.

Three objectives of this ESA-funded programme are to:

1. Synthesise and characterise surrogates for different americium oxides and establish the effect of varying the synthesis parameters on the particle

³ Reprinted from Journal of Nuclear Materials, Vol 320, Chemical Thermodynamic Representation of AmO_{2-x} , Pages 292-298, Copyright (2003), with permission from Elsevier.

characteristics, such as shape and size. The key motivation is to be able to create oxide particles with different characteristics without the need for ball-milling the powder. Ball-milling should be avoided for radiological protection reasons. Micron-sized (micrometric) material is therefore targeted to avoid respirable fine production. A first step will be to understand how varying the parameters of the oxalate precipitation process influence the characteristics of the oxalate particles.

2. Compare and assess how surrogates for different americium oxides sinter under different sintering environments. This includes comparing different sintering techniques and assessing, for example, pellet/disc relative density and changes in composition and crystal structure. Volume changes associated with crystallographic phase transitions may want to be avoided during sintering as this could, for example, impact densification (see Chapter 5 for further details).
3. Compare the impact of varying the particle characteristics, such as shape and size, of the input surrogate materials on sintered pellet properties e.g. relative density and mechanical integrity.

3. How this Thesis Complements the ESA RPS Programme

In this thesis a Ce Nd oxide solid solution phase, namely $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$, is proposed as a potential surrogate for a substoichiometric cubic form of americium, $\text{AmO}_{2-(x/2)}$, namely the C' region presented in Figure 1.5. Using a mixed oxide should provide a greater diversity of surrogate options for americium oxides with different oxygen-to-metal ratios (x-values) in future sintering trials e.g. other than $\text{CeO}_{2-(x/2)}$. The $\text{CeO}_{2-(x/2)}$ species can also readily re-oxidise under ambient conditions (see § 1.2.1 in Chapter 5).

The ability to synthesise this Ce Nd oxide material with a reproducible x-value using an oxalate coprecipitation and calcination technique is demonstrated. The effect of the precipitation temperature on oxalate particle properties such as size is investigated as a stepping stone to fabricating the oxide material with different particle properties for future sintering trials (see the third ESA early fuel development objective in § 2.3).

Another focus of this thesis was to investigate and compare the sintering behaviour of CeO_2 using two different techniques: spark plasma sintering (SPS) and cold-pressing-and-sintering, to inform ESA's decision on how AmO_2 could be sintered. As the current synthesis method creates AmO_2 with lath-shaped morphology (see Figure 1.6), batches

of lath-shaped CeO_2 with different particle sizes and specific surface⁴ areas (Sarsfield et al., 2016a) have been sintered to address the third ESA early fuel development objective that is outlined in § 2.3. The ability to achieve intact sintered bodies with densities in the ~85-90 % T.D. range is assessed and the mechanical hardness is compared between the different samples. Additionally, Nd_2O_3 has also been spark plasma sintered to provide an initial indication of how Am_2O_3 may sinter.

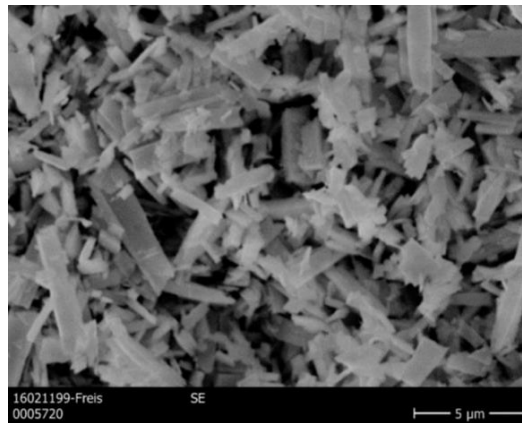


Figure 1.6: Illustrates the lath-shaped morphology of AmO_2 generated by the ESA chemical flow sheet (Sarsfield et al., 2016a). See § 3 of Chapter 2 for more details.

Finally, in preparation for using the synthesised Ce Nd oxide for future sintering studies, the material has undergone detailed X-ray diffraction analysis using Rietveld refinement to establish the lattice parameter precisely and to infer the x-value from this parameter. By characterising the material's crystallographic properties in this way, this data can be used in future sintering investigations as a starting point for establishing the effect of sintering processes on changes in the material's crystal structure (the second ESA early fuel development objective). Additionally, the lattice parameter is used to infer the x-value of the material to see if this corroborates with the value targeted with the oxalate co-precipitation process and with the quantitative X-ray fluorescence (QXRF) determined value from the earlier study in Chapter 5. The QXRF analysis only measured the Ce and Nd ion concentrations.

⁴ This material was fabricated using an oxalate precipitation and calcination technique by the National Nuclear Laboratory. Further details are found in Sarsfield et al. (2016a) and Chapter 6 of this thesis.

3.1. Thesis Outline

Chapter 2 provides a general overview of the oxalate precipitation and calcination process for oxide fabrication. As well as outlining the ESA chemical flow-sheet for creating americium oxides, it reviews the literature on relevant actinide and surrogate oxalate precipitation experiments. This establishes the variables that have been investigated in past experiments and which variables have had the greatest impact on oxalate and oxide particle properties. The findings influenced the choice for the Ce Nd oxalate coprecipitation and calcination investigation in Chapter 5.

Chapter 3 describes some sintering theory and provides an explanation of the two sintering techniques that have been compared in this thesis: spark plasma sintering (SPS) and cold-pressing-and-sintering. Literature on the SPS and cold-press-and-sinter of CeO_2 and Nd_2O_3 are reviewed to inform the sintering studies of micrometric material and the lath-shaped micrometric CeO_2 , which are presented in Chapter 6. With the primary focus being on CeO_2 sintering studies, the review is focussed on CeO_2 related literature. With limited studies on the SPS of CeO_2 , literature on UO_2 is also reviewed (see Chapter 3 for more details). Vickers hardness is found to be one of the few mechanical properties of nuclear ceramics that is commonly reported.

Chapter 4 describes the various analytical techniques that have been used in this thesis with an introduction to some basic theory. An introduction into the hardness testing of ceramics is also provided with a focus on Vickers hardness testing.

Chapter 5 outlines the aforementioned cerium neodymium oxalate co-precipitation and calcination experiment to fabricate $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$.

Chapter 6 presents the multi-faceted sintering study that compares the SPS and cold-press-and-sinter of CeO_2 to establish if intact sintered bodies with relative densities between around 85-90 % T.D. can be achieved. Microstructures and the Vickers hardness values are compared. The ability to SPS a pellet with a geometry nominally representative of a ~3 Wt RHU pellet is also explored. Lath-shaped CeO_2 is sintered and the impact of particle size and specific surface area on sintering and Vickers hardness behaviour is assessed. Neodymium(III) oxide is also spark plasma sintered using a range of different sintering profiles.

In preparation for the potential use of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ oxide for future sintering studies (its fabrication is described in Chapter 5), Chapter 7 outlines the detailed powder X-ray diffraction analysis study using Rietveld refinement to precisely determine its lattice parameter and to infer its x-value for comparison with previous QXRF data and the targeted x-value.

Chapter 8 summarises the findings of this thesis and presents some future avenues of research that would benefit the ESA RPS Programme's fuel development research.

CHAPTER 2:

BACKGROUND AND THEORY BEHIND WET CHEMICAL NUCLEAR FUEL PROCESSING

1. Introduction

The properties of a sintered pellet such as density and microstructure can be influenced by the morphology and size of the input oxide powder, as well as by the sintering process used to consolidate the powder. For example, Smith et al. (1976) noted that the morphology of PuO_2 particles affected the microstructure of hot-pressed-and-sintered PuO_2 . Smith et al. (1976) used the oxalate precipitation (Pu(III) oxalates) and calcination technique to fabricate the input oxide material. The technique has vast heritage (see § 2) and allows oxide particles of different morphologies and sizes to be synthesised by varying the parameters of the precipitation and calcination steps (see § 1).

Americium oxide pellets will be fabricated in the ESA RPS programme using oxide material synthesised by oxalate precipitation and calcination (see § 3). The sintering studies require an understanding of how surrogate oxide and americium oxide particles could be fabricated with different particle characteristics such as morphology and size. As was eluded to in Chapter 1, one purpose of this study was to establish how Ce Nd oxalate particles with differing particle characteristics could be created. When calcined, the oxalates would be converted to oxides. This investigation would be a step towards making Ce Nd oxide solid solutions with differing particle characteristics. In this thesis, these oxides have been proposed as surrogates for certain substoichiometric americium oxides i.e. $\text{AmO}_{2-(x/2)}$ where x is a fraction between 0 and 1 (inclusive).

An overview of the oxalate precipitation and calcination process for oxide fabrication is provided in § 2 of this chapter, which is followed (in § 2) by a brief description of the method for creating americium oxide fuel for ESA RPSs. This method describes the process for producing AmO_2 (see § 3) but an insight into how $\text{AmO}_{2-(x/2)}$ phases could be fabricated is also provided. Finally, the literature on Am(III), Pu(III), Pu(IV), and Ce(III) oxalate precipitations (from nitrate feed inputs) is reviewed in § 4 of this chapter to establish which precipitation variables have previously been investigated and which had the greatest influence on oxalate particle characteristics such as morphology and size.

The ESA programme identified cerium as a suitable chemical and crystallographic surrogate for americium oxide fabrication. Cerium oxalate precipitation has been used to simulate the plutonium system in the past. The United States (U.S.) conducted numerous extensive plutonium oxalate precipitation and calcination investigations as part of the RPS PuO₂ production process research. Rather than presenting the quantitative details of the findings outlined in the literature, general trends are presented in § 3. This is because the specific values for certain particle characteristics e.g. particle size, may differ between plutonium, cerium and cerium neodymium oxalate precipitation experiments owing to differences in chemistry. For this reason, the values for the oxalate precipitation variables, such as the nitric acid concentration, used in each of the reviewed experiments are not included in this chapter. The reader is referred to the referenced articles for specific quantitative details, but some examples are provided in Appendix A for the readers' reference. The findings of this review have been used to inform the decision on which parameters would be varied in the Ce Nd oxalate precipitation experiments to investigate their influence on oxalate particle characteristics such as size. This investigation is outlined in Chapter 5.

2. Oxalate Precipitation and Calcination: an overview

Oxide fabrication by the calcination of precipitated oxalates is a well-established technique (Sarsfield, 2015). In the context of plutonium production, the heritage of the technique dates back over 60 years to the Manhattan Project when Los Alamos laboratory developed the oxalate precipitation process, which was later tested at Hanford site (Facer Jr. and Harmon, 1954-Declassified with Deletions in 1962, Sarsfield, 2015). The reprocessing of spent nuclear fuel allows actinides of interest to be extracted (Simpson and Law, 2010). In the case of plutonium, oxalate precipitation has enabled it to be processed into a pure form (Sarsfield, 2015). Oxalate precipitation and calcination is already used on an industrial scale e.g. by the civil nuclear power industry when reprocessing spent (uranium) reactor fuel via the plutonium uranium redox extraction (PUREX) method (Gill et al., 2014).

In the context of nuclear fuels, oxalate precipitation is the result of a chemical reaction between, typically, metal nitrates or chlorides (in nitric acid) and an excess of oxalic acid (Sarsfield, 2015, Horlait et al., 2011). In this process, the metal oxalate reaction product is precipitated (see Glossary) from solution as a solid once the supersaturation limit has

been reached. The suspended solid oxalate precipitate is then filtered from the remaining fluid, which is known as the mother liquor, and the resultant ‘cake’ material is dried. After drying, the actinide and lanthanide oxalates typically remain hydrated to some extent.

The oxalate ‘cake’ is heated in a furnace to several hundred degrees Celsius to decompose the oxalate into an oxide. Carbon monoxide and carbon dioxide are released during this process. The oxalate is often heated in an air atmosphere. However, the decomposition atmosphere can dictate the final oxide form for certain oxalates. For example, Am(III) oxalate will decompose to AmO₂ in air but into Am₂O₃ in a vacuum (Markin, 1958) as shown in the thermogravimetric analysis (TGA) curves in Figure 2.1, which were recorded using a 3 °C min⁻¹. The TGA method can be used to monitor oxalate dehydration and decomposition.

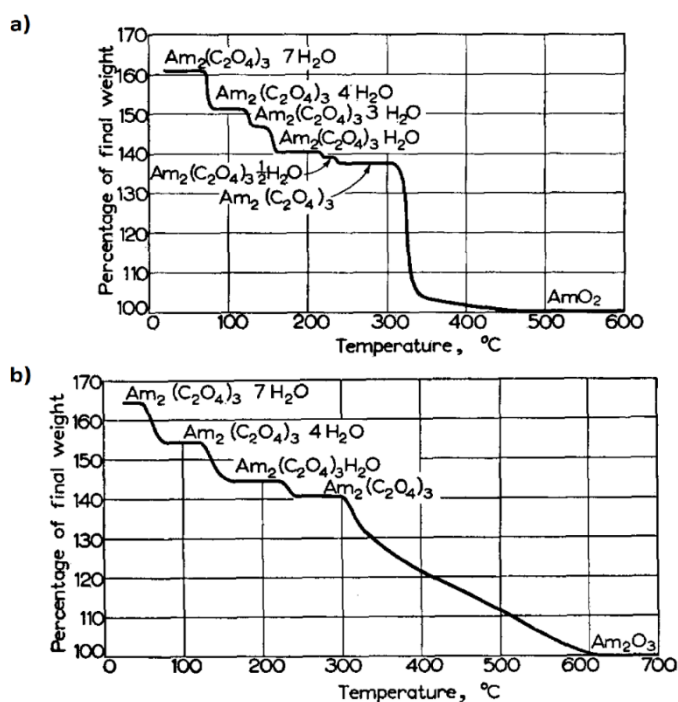


Figure 2.1: TGA data for Am(III) oxalate dehydration and decomposition a) in air and b) in vacuum (Markin, 1958).⁵

⁵ Reprinted from Journal of Inorganic and Nuclear Chemistry, 7, T. L. Markin, The thermal decomposition of americium (III) oxalate, 290-291, Copyright (1958), with permission from Elsevier.

3. Chemical Flow-sheet for Synthesising Americium Dioxide

As was noted in Chapter 1, the United Kingdom has a stored supply of reprocessed separated plutonium with ‘in-grown’ americium at the Sellafield Ltd. site in Cumbria. This plutonium is in powdered PuO_2 form (The Royal Society, 2007). As part of the ESA space nuclear power research programme, a chemical flow-sheet has been developed for the process of extracting ^{241}Am from the PuO_2 material and converting it into oxide powder (Sarsfield, 2013, Sarsfield et al., 2015). The americium oxide material would be used as feedstock for sintering trials to fabricate pellets or discs. A schematic of the flow-sheet is illustrated in Figure 2.2, which illustrates the method for AmO_2 synthesis.

As was mentioned in Chapter 1 in § 2.2, the oxygen-to-metal ratio and crystallographic form of the final americium oxide pellet for an RPS or RHU is yet to be decided in the programme. If a substoichiometric oxide form is required, e.g. $\text{AmO}_{2-(x/2)}$ where $0 < x \leq 1$, then one of two options could be pursued:

1. Reduce (see Glossary) the AmO_2 powder and then sinter it into a pellet. This would require an additional processing step in Figure 2.2, which is shown in a dashed box.
2. Sinter AmO_2 into a pellet and then reduce the pellet.

Regardless of the method, the AmO_2 (pellet or powder) would need to be heated in a thermobalance where the temperature and the gaseous environment, such as the hydrogen content, would be controlled to provide the appropriate reducing conditions to target particular oxygen-to-americium ratios (Sari and Zamorani, 1970) or x-values.

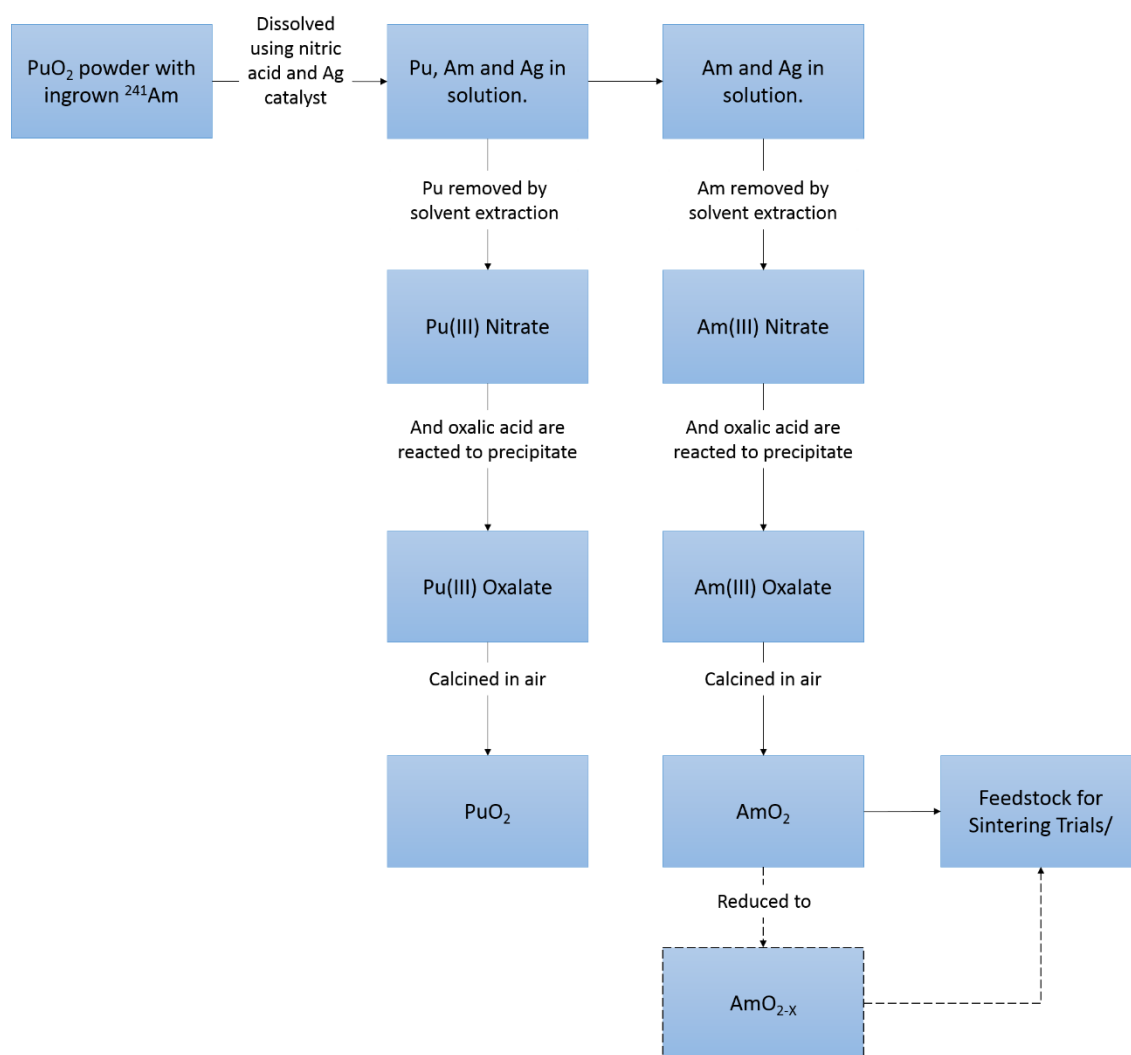


Figure 2.2: The ESA Americium chemical flow-sheet. Image adapted from (Sarsfield et al., 2015, Sarsfield, 2013).

4. Tuning Oxalate and Oxide Particle Characteristics

In the context of actinide oxide fuels and their lanthanide surrogates, there have been several studies that highlight that oxalate particle morphology and size are dictated by the parameters of the oxalate precipitation process. This literature review only focuses on experiments where actinide/lanthanide nitrates dissolved in nitric acid and oxalic acid have been reacted (as opposed to chloride and oxalic acid reactions, which have been investigated by others e.g. Horlait et al. (2011)) as these are most relevant (see Figure 2.2).

It has been well documented that oxalate particles typically maintain their morphology on calcination to oxide form, which has highlighted the importance of the oxalate precipitation chemical process in dictating oxide morphology.

The calcination atmosphere will influence the oxygen-to-metal ratio of the final oxide, and the temperature will impact the residual carbon content as well as the porosity and specific surface area of the oxide particles.

4.1. Americium Oxalate Precipitation in the Literature

Only one published study on americium(III) oxalate precipitation exists in the literature: a direct strike $^{243}\text{Am(III)}$ oxalate precipitation experiment by Smirnova et al. (1988). Direct strike is a term used in the nuclear industry that refers to the order of addition of the reactants. In this context, it means that oxalic acid has been added to the metal nitrate solution, whereas reverse strike refers to the addition of metal nitrate solution to oxalic acid (see the Glossary).

Smirnova et al. (1988) studied the impact of changing the nitric acid concentration, oxalic acid addition rate, precipitation temperature and aging time (also known as digestion time; see Glossary) on oxalate particle morphology and size. They investigated the impact of changing one or multiple precipitation variables at a time. The conditions and results of their experiments are reprinted in Table 2.1 (note this spans over two pages).

Their results showed that the morphology of the oxalate particles were dependent on the nitric acid concentration, oxalic acid addition rate, and precipitation temperature. Morphologies, which varied according to the exact conditions used, included:

- mixtures of platelets
- needles and dendrites
- platelets and needles
- platelets
- “porcupine”-like aggregates of needles, which is shown in Figure 2.3.

Although the image quality of the latter presented by Smirnova et al. (1988) is not ideal, it is queried whether some of the porcupine particles i.e. the spherical-like particle illustrated on the left in Figure 2.3, could have had similar morphology to rosette PuO_2 materials created by via direct strike (see § 4.3.1 and Figure 2.5) by Burney and Congdon

(1982). Smirnova et al. (1988) found that an increase in digestion time did not generally impact particle morphology, except for one experiment (see run 2 in Table 2.1) where dendrite particles were no longer present after 7 days of aging. However, an increase in digestion time, generally resulted in an increase in particle size.

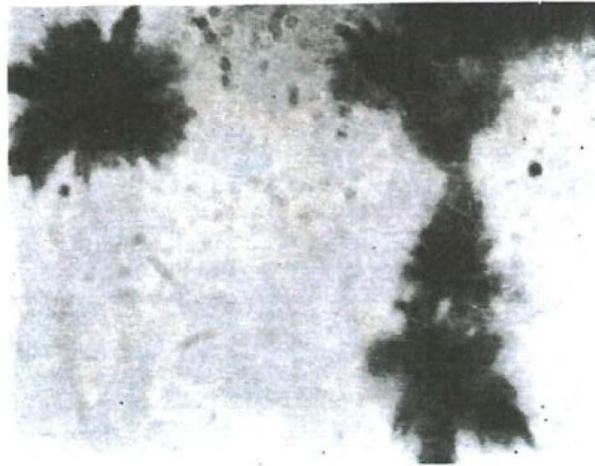


Figure 2.3: Am(III) oxalate ‘porcupine’-like particles observed by Smirnova et al. (1988).

Table 2.1: The Am(III) oxalate precipitation results of Smirnova et al. (1988).

No. of run	Experimental conditions	Size and shape of crystals when held in mother liquor for the time (days):		Am content in soln, mg/liter, when held for the time (days):	
		1	7	1	20
1	Starting soln (1 ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter, [HNO ₃] = 0.1 moles/liter Precipitating agent (0.14 ml) [H ₂ C ₂ O ₄] = 0.9 moles/liter T = 75 ± 1°C	Platelets of length 20-30 µm; width 3-6 µm; thin, transparent Thin, needle-shaped crystals, length 30 µm, width < 1 µm Dendrites	No change	4.45	2.42
2	Starting soln (1 ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter, [HNO ₃] = 0.44 moles/liter Precipitating agent (0.5 ml) [H ₂ C ₂ O ₄] = 0.9 moles/liter, T = 75 ± 1°C	Platelets of length 50-90 µm; width 3-6 µm; thin, transparent Thin, needle-shaped crystals; length 90 µm, width ~1 µm Dendrites	Platelets of length 50-90 µm, width up to 15 µm Number of needle-shaped crystals decreased	3.98	2.09
3	Starting soln (1 ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter, [HNO ₃] = 0.5 moles/liter, Precipitating agent (0.5 ml) [H ₂ C ₂ O ₄] = 0.9 moles/liter, T = 75 ± 1°C	Similar to run 2	Similar to run 2	4.20	2.21
4	Starting soln (1 ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter, [HNO ₃] = 1.0 moles/liter Precipitating agent (1.0 ml) [H ₂ C ₂ O ₄] = 0.9 moles/liter, T = 75 ± 1°C	Platelets of length 20-30 µm; width 6 µm; thin, transparent Needle-shaped crystals, length 30-45 µm, width 1 µm	Platelets of length 40 µm, width 9 µm	3.70	2.44
5	Starting soln (1 ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter, [HNO ₃] = 0.5 moles/liter Precipitating agent (5 times, 0.1 ml each) [H ₂ C ₂ O ₄] = 0.9 moles/liter, T = 75 ± 1°C	Inhomogeneous platelets, length 50-100 µm, width 20-30 µm	Nontransparent platelets, length 50-240 µm, width 30 µm, thickness 3-5 µm	3.39	2.43
6	Starting soln (1 ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter, [HNO ₃] = 0.44 moles/liter Precipitating agent (0.5 ml) [H ₂ C ₂ O ₄] = 0.9 moles/liter, T = 20°C	Aggregates of small needle-shaped crystals, 15-30 µm in shape of "porcupines"	Aggregates of small crystals 20-30 µm	3.26	1.83

Table 2.1 (continued): The Am(III) oxalate precipitation results of Smirnova et al. (1988).

No. of run	Experimental conditions	Size and shape of crystals when held in mother liquor for the time (days):		Am content in soln, mg/liter, when held for the time (days):	
		1	7	1	20
7	Starting soln (1ml) [Am] = $7.6 \cdot 10^{-3}$ moles/liter [HNO ₃] = 0.44 moles/liter Precipitating agent (5 times, 0.1 ml each) [H ₂ C ₂ O ₄] = 0.9 moles/liter, T = 20°C	Similar to run 6	Similar to run 6	6.40	3.17

4.2. Cerium(III) Oxalate Precipitation

Cerium(III) oxalate precipitation has been used as a chemical surrogate for Pu(III) oxalate precipitation and as a surrogate for Am(III) oxalate precipitation as part of the ESA programme. An extensive study by Li et al. (2009) showed that cerium oxalate particle size was influenced by the parameters of the precipitation process. In their investigation, Li et al. (2009) reacted cerium(III) nitrate and oxalic acid chemical feeds simultaneously to continuously precipitate Ce(III) oxalates. They systematically investigated the impact of cerium(III) nitrate concentration, oxalic acid concentration, feed rate, mixing rate and reaction temperature on oxalate particle size and in some instances, particle morphology. However, the impact of varying the concentration of only one reactant was not investigated. To maintain a desired stoichiometry, Li et al. (2009) varied the concentration of the oxalic acid according to the nitrate feed concentration. The details of the rationale were not provided. The experimental set-up comprised two vessels: a smaller vessel where the initial reaction and precipitation took place, and a larger vessel where the precipitates were left to age. Both vessels contained stirrers and the contents of the smaller vessel fed into the larger vessel.

An increase in cerium (III) nitrate and oxalic acid concentrations resulted in a decrease in median particle size and in the width⁶ of the particle size distribution. However, when the concentrations were sufficiently high, the median particle size increased (the width

⁶ Li et al. (2009) define the width R by the following equation: $R = (d_{90} - d_{10})/d_{50}$. The definitions of these terms are provided in Chapter 4, which provides an introduction to particle size analysis.

continued to narrow; see Appendix A). Li et al. (2009) attributed this change of trend to considerable particle agglomeration.

Their investigation found that an increase in mixing rate (from 200 to 400 revolutions per minute, RPM) resulted in a decrease in median particle size, but a further increase (to 500 RPM) resulted in a particle size increase (see Appendix A). The width of the distribution fluctuated with an increase in mixing rate. Li et al. (2009) stated that mixing aids the diffusion of the ions, but it can result in particle breakage if it is too vigorous.

Owing to the continuous nature of the precipitation, the aging (digestion) time was dictated by the feed rates of the reactants. Median particle size decreased with an increase in feed rate but the particle size distribution width decreased. Li et al. (2009) stated that the reduction in particle size was a consequence of a reduction in aging time, which did not allow particle growth.

Reaction temperature was also found to affect oxalate particle size (Li et al., 2009): particle size increased with an increase in reaction temperature but the particle size distribution fluctuated slightly. They noted that smaller particles were created at lower temperatures as a consequence of a higher nucleation rate than growth rate, but the opposite effect occurred at higher temperatures resulting in larger particles. The oxalate particles had a “sheet” morphology regardless of the temperature at which they were precipitated as shown in Figure 2.4 (Li et al., 2009).

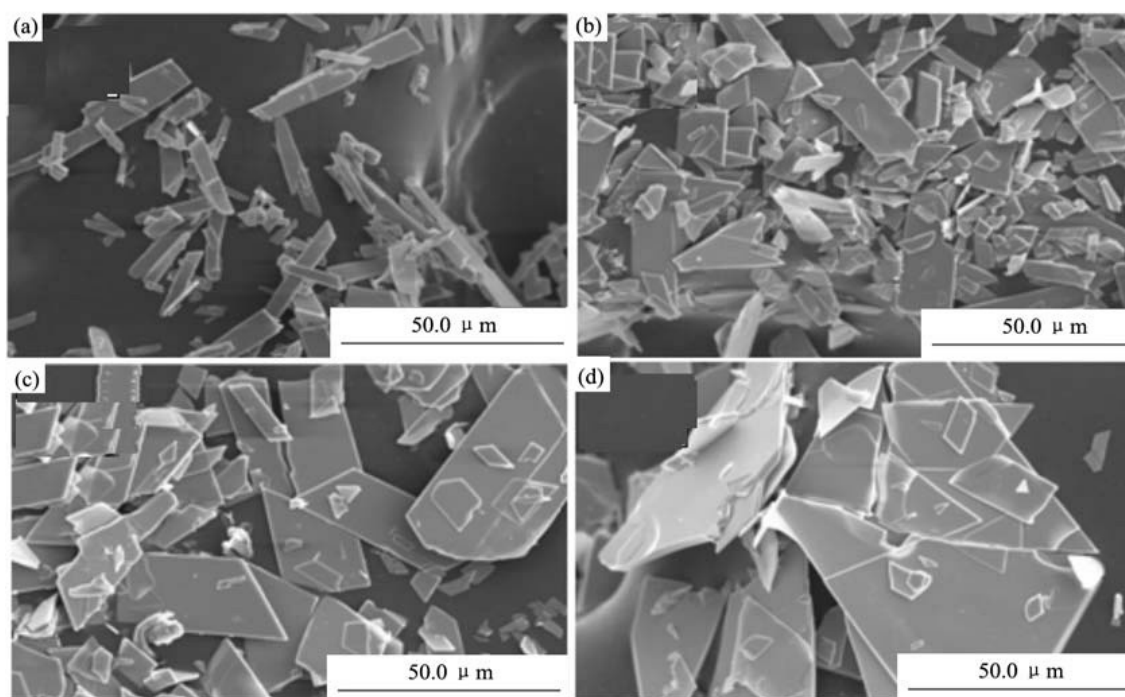


Figure 2.4: Cerium oxalate particles precipitated by Li et al. (2009) at a) 25 °C; b) 40 °C; c) 60 °C and d) 80 °C.⁷

4.3. Plutonium Oxalate Precipitation for U.S. RPSs

There have been several detailed studies on the effect of varying Pu(III) and Pu(IV) oxalate precipitation process parameters, such as precipitation temperature, on oxalate and oxide particle size and morphology (Rankin and Burney, 1974, Smith et al., 1976, Burney and Congdon, 1982, Burney and Smith, 1984). There have been a number of investigations on the influence of PuO₂ particle morphology, size and post-processing (e.g. milling) on sintered pellet properties such as density and microstructure. These studies were vital to the development of the PuO₂ pellet fuel form now used in US radioisotope thermoelectric generators and heater units. The number and complexity of these studies highlight the importance of understanding the impact of the oxalate precipitation process on the properties of the oxide final pellet and why such investigations are essential to the ESA americium oxide fuel form development research. However, a comprehensive literature review of these findings is beyond the scope of this

⁷ Reprinted from Journal of Rare Earths, 27, M. Li et al., Cerium dioxide with large particle size prepared by continuous precipitation, 991-996, Copyright (2009), with permission from Elsevier.

thesis and only elements most relevant to near-term ESA fuel development studies are discussed.

4.3.1. Direct Strike

4.3.1.1. Reactant Addition Rate

Rankin and Burney (1974) conducted a comprehensive study on the impact of changing the variables of direct strike Pu(III) oxalate precipitation on the resultant PuO₂ particle size distribution and morphology. They investigated the impact of the acid addition rate and the reagent mixing rate on particle characteristics made by the direct strike method (see Glossary). In general, they found that an increase in oxalic acid addition rate resulted in a decrease in median oxalate and corresponding oxide particle sizes (see Appendix A). Rankin and Burney (1974) noted that the exact median values were affected by precipitator and paddle design, stirring rate of the paddle, and the plutonium concentration. The former two affected mixing (Rankin and Burney, 1974).

4.3.1.2. Reactant Mixing Rate

Rankin and Burney (1974) stated that the reagent mixing rate had a smaller impact on particle size than the order of reagent addition. They found that if the rate was too high, then agglomerates and particles would break resulting in a reduced median particle size (Rankin and Burney, 1974). However, the rate needed to be sufficiently large to allow particles to grow (Rankin and Burney, 1974). If the rate was too low, particles would not suspend and grow. Rankin and Burney (1974) noted that insufficient mixing may have affected particle morphology. On observation of the figures, this could have corresponded to less agglomeration but the image quality is poor, which makes judgement difficult.

It was also found that the longer the time interval between manufacture and inspection, the smaller the median particle size became e.g. after around 16 months the particle size decreased by 90 % (no quantitative data were noted in the study by Rankin and Burney (1974) to enable specific details to be provided in Appendix A)

4.3.1.3. Vessel Design, Mixing Rate, Digestion Time, Nitric Acid Concentration and Temperature

In a later study by Smith et al. (1976), particle morphology and size was found to be unaffected by the precipitator design, stirring rate and digestion time. They conducted reverse strike and direct strike studies. Smith et al. (1976) stated that an increase in

particle size resulted from an increase in precipitation temperature and that agglomeration or aggregation lessened with this temperature increase (Smith et al., 1976). Particle size also increased with an increase in nitric acid concentration and produced spherulites (Smith et al., 1976). However, it was not clear for which method of acid addition (direct strike or reverse strike) these trends had been observed. Smith et al. (1976) clearly stated that the direct-strike route resulted in increased agglomeration and aggregation, with aggregated morphologies such as spherulites and rosettes. They did not provide illustrations of the spherulite and rosette particles.

4.3.1.4. Two-Step Direct Strike and Vessel Design and Reaction Temperature

In 1982, Burney and Congdon (1982) reported a method to create Pu(III) oxalate rosette agglomerates that when calcined to PuO₂ could be used as a direct feedstock to hot-press pellets for General Purpose Heat Sources (GPHSs). They used a two-step direct strike method where the oxalic acid concentration was adjusted twice. They investigated how the precipitation parameters affected particle morphology and size.

Two different precipitator designs were used in their investigations: one was made of glass and allowed 1 g precipitation and the other of stainless steel and allowed 5 g precipitation. The reader is referred to the report by Burney and Congdon (1982) for further details of the designs and hence differences between the two precipitators. Rosette aggregates that were 60 to 100 µm in size (comprising closely packed 2 to 3 µm platelets) were created using the 1 g precipitation vessel. These particles are illustrated in Figure 2.5. When the process was repeated with the larger vessel, aggregate particles with a more constrained size but same morphology were made (50 to 60 µm).

An increase in precipitation temperature (from 23 °C to 35 °C) as well as addition and digestion times and or method (i.e. the amount of oxalic acid added per step) affected aggregate morphology in different ways e.g. an increase in temperature resulted in loosely packed laths (see Glossary) with attached aggregates of smaller platelets, resulting in a “[g]enerally not spherical” rosette morphology (Burney and Congdon, 1982). These particles are illustrated in Figure 2.6. On decreasing the temperature to 15 °C, all precipitated aggregates were spherical regardless of the addition and digestion times and or methods used. However, a change in these variables affected the size of the aggregates and the constituent platelets.

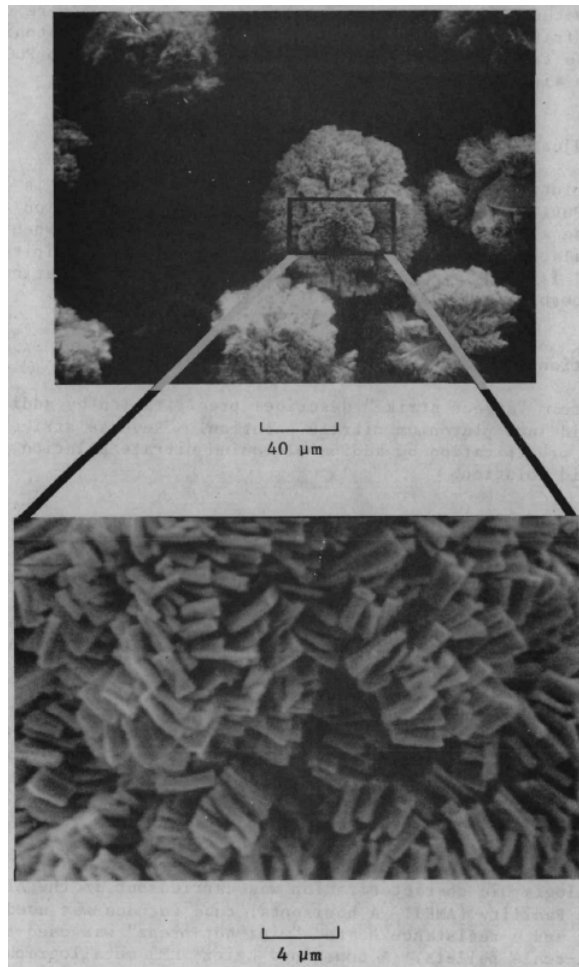


Figure 2.5: Pu(III) oxalate rosettes synthesised using a two-step direct strike method by Burney and Congdon (1982).⁸

⁸ In accordance with image reuse guidance, the following information is provided: the research conducted by Burney and Congdon (1982) at Savannah River Laboratory (as it was known as then) was prepared under a U. S. Department of Energy contract, namely, DE-AC09-76SR00001.

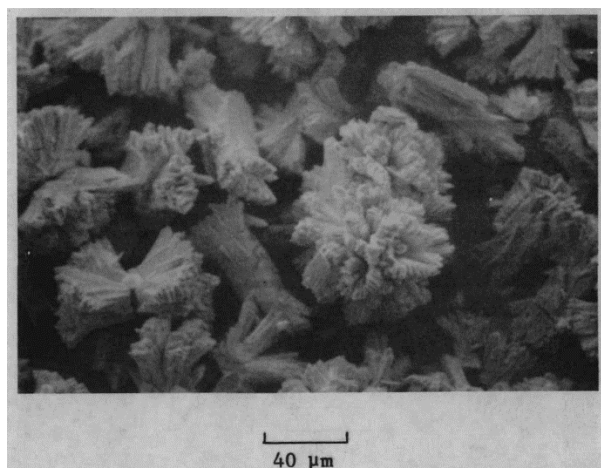


Figure 2.6: Illustrates the “Generally not spherical” PuO_2 rosettes that were made using a direct strike method (Burney and Congdon, 1982).⁸

4.3.2. Direct Versus Reverse Strike

Rankin and Burney (1974) found that oxides derived from oxalates precipitated by the direct strike method resulted in PuO_2 particles with a larger median size ($\sim 30 \mu\text{m}$) than those precipitated by reverse strike (around 3 to 9 μm median size depending on the batch). The order of reagent addition also had a major impact on the respirable fine fraction. They defined particles under 4 μm in size as respirable when this study was undertaken. Less than 5 % of PuO_2 particles were of respirable size when derived from direct strike oxalates, but 30 to 60 % of PuO_2 particles were respirable in size when derived from reverse strike oxalates (it is assumed that the range corresponded to batch-to-batch variation). See the Glossary for an updated definition.

4.3.3. Reverse Strike

Burney and Smith (1984) made $^{238}\text{PuO}_2$ by calcining Pu(III) oxalates precipitated by the reverse strike method and investigated the influence of the precipitation parameters on the resultant $^{238}\text{PuO}_2$ particle characteristics. The morphologies of the oxalate particles were either laths or agglomerates of laths. On calcination the oxides maintained their morphology i.e. the calcination process was a pseudomorphic transformation. The particle size distribution of the oxalate particles was bimodal, with the modes corresponding to individual laths and the agglomerates. The shape of the distribution was maintained for the oxides. However, the agglomerates were considered loosely bound as they separated into their constituent laths on prolonged ultrasonication in their suspension fluid (suspension was needed for the particle size analysis).

4.3.3.1. Temperature and Reagent Concentrations

Burney and Smith (1984) found the PuO_2 particle size was dictated by the oxalate reverse strike precipitation reagent concentrations and temperatures. Factors that caused an increase in particle size were an increase in nitric acid concentration and an increase in precipitation temperature (via an Arrhenius equation). The latter also caused an increase in each of the three dimensions (length, width and thickness) of the lath particles, whereas an increase in nitric acid concentration affected the three aspect ratios differently (The reader is referred to the study by Burney and Smith (1984) for further details.).

Factors that caused a decrease in particle size were a decrease in oxalic acid concentration and an increase in the plutonium concentration in the Pu nitrate in nitric acid feed at elevated temperatures (above room temperature).

Their analysis suggested that less agglomeration occurred as the precipitation temperature increased. Burney and Smith (1984) postulated that this was because fewer particles existed at higher temperatures, which meant they were less likely to coalesce as agglomerates. Their analysis suggested that the agglomerates did not form via nucleated agglomerated clusters nor via dendrites but instead formed as coalesced laths.

However, Burney and Smith (1984) did find that if the nitric acid concentration was increased to a sufficiently high level (5 M), then spherulite agglomerates were formed. These agglomerates were the result of laths growing from a common nucleation site owing to the fast growth rate. The U.S. RPS programme did not use the spherulite particles to create PuO_2 pellets.

4.3.4. Conclusion of the Pu Oxalate Precipitation Literature Review

The plutonium investigations highlight that there are many variables in the oxalate precipitation process but some have a greater impact on particle size and morphology than others. The particle morphology and the particle size distribution are dictated by the specific values of these variables. The combination of each of the variables dictate the result. The order of reagent addition is also influential (This cannot be dictated by a value.).

5. Context for the ESA Programme

One of the ESA programme objectives for the surrogate oxide sintering investigations was to establish the impact of particle characteristics such as size and morphology on sintered body properties such as density and mechanical properties. With the initial sintering studies focussing on CeO_2 as a surrogate for AmO_2 , batches of CeO_2 with different particles sizes and specific surface areas were made by Sarsfield et al. (2016) as part of the wider ESA programme. All particles had lath morphology. These characteristics were dictated by the Ce(III) oxalate precipitation and calcination (temperature) conditions used to make them (Sarsfield et al., 2016). These CeO_2 batches were used in the sintering investigation described in Chapter 6 of this thesis.

In this thesis, Chapter 5 describes a Ce Nd oxalate precipitation and calcination experiment. One of the objectives of the experiment was to establish whether oxalate particles could be synthesised with different particle morphologies and sizes. The synthesis method was involved reacting a Ce and Nd nitrate (III) mixture with oxalic acid to co-precipitate oxalate coprecipitates, which would be calcined to create Ce Nd oxide solid solutions. By starting from a metal nitrate feed, comparisons could be made with the cerium oxalate precipitation (Sarsfield et al., 2016) and future americium oxalate precipitation studies in the ESA programme. A similar precipitation vessel design to the Ce oxalate study was used for the Ce Nd oxalate investigation. The experiment allowed continuous precipitation over several hours and the reactants were added to the vessel continuously at the same feed rates as used in the initial Ce oxalate precipitation investigation. The same acid concentrations were also used. The effect of precipitation temperature on Ce Nd oxalate particle morphology and size was investigated as part of this study. The methods, results and discussion of these results are outlined in Chapter 5.

It is highlighted that prior to this study, Higashi et al. (1998) provided the only known published work on co-precipitation of Ce Nd oxalates from the reaction of a cerium and neodymium (III) nitrate mixture and oxalic acid. They used a reverse strike method (the nitrate feed was added to the oxalic acid). Although their investigation included cerium neodymium oxalate precipitation work (with x equal to 0.2) they did not present particle size analysis results nor images showing the oxalate morphology.

CHAPTER 3:

SINTERING OF NUCLEAR FUELS AND THEIR SURROGATES: BACKGROUND AND CONTEXT

1. Introduction

The americium oxide fuel powder will need to be sintered into a single consolidated structure, such as a pellet, that can be integrated into an RPS. The sintered structure will need to remain structurally intact during RPS integration as well as during the launch and initial phases of a space mission. The early requirements of the americium oxide fuel for the ESA RPS programme were outlined in § 2.1 of Chapter 1.

The cold-press-and-sinter ceramic processing technique is a well-established method that is used by the nuclear industry. It was used in the early studies for the United States' PuO_2 fuel development for space radioisotope power systems (see § 4.4). Recent U.S. RPS fuel powder processing has involved hot pressing (Borland et al., 2009). There is limited experience and knowledge of using the spark plasma sintering (SPS) technique to sinter nuclear materials for space radioisotope power systems or space reactor fuels (O'Brien et al., 2009, Williams et al., 2013). However, the method has gained some light in the civil nuclear industry e.g. where UO_2 pellets made by SPS have been compared to those fabricated with conventional sintering methods (Ge et al., 2013).

This chapter begins (§ 2) with a brief introduction into sintering theory and is followed by a description and comparison of the two sintering techniques considered for this study: spark plasma sintering (SPS) and the cold-press-and-sinter technique. The chapter then proceeds with a literature review (§ 3) to understand how CeO_2 and Nd_2O_3 may spark plasma sinter. There are very few SPS studies on pure CeO_2 reported in the literature (Choi et al., 2010, Choi et al., 2012). The literature review therefore includes SPS studies of CeO_2 as a surrogate for $\text{UO}_2/\text{PuO}_2/\text{NpO}_2$. It was decided that the SPS studies on UO_2 were relevant (particularly as CeO_2 is used as surrogate for UO_2) and could help in understanding trends when processing ceramic powders. Where possible, the impact of the SPS parameters on pellet density and mechanical properties are described.

At the time of commencing this study, no spark plasma sintering investigations on pure Nd_2O_3 had been reported in the public literature. In § 4, the literature on the

cold-pressing-and-sintering of CeO_2 and Nd_2O_3 is reviewed, and a brief description of what could be expected from the cold-pressing-and-sintering of lath-shaped material is also provided. Specifically, a study on the cold-press-and-sinter of lath-shaped PuO_2 is reviewed (Bickford et al., 1976). However, it is noted that there could be differences in how lath-shaped AmO_2 and lath-shaped PuO_2 sinter. Finally, in § 5, the findings of the review that are relevant to this doctoral thesis study are summarised. This chapter provides the context for the comparative study on the SPS and cold-press-and-sinter of micrometric CeO_2 as well as for the SPS sintering investigation with micrometric Nd_2O_3 . These investigations are outlined in Chapter 6.

2. Sintering Theory and Technique Comparison

Sintering is an irreversible process that acts to reduce the free energy of the system using a number of methods known as driving forces, namely, chemical reactions, pressure application and surface free energy reduction (Rahaman, 2007). The primary driving force in sintering is surface free energy reduction, which is achieved internally within the sintering body by decreasing the grain surface area (De Jonghe and Rahaman, 2003).

Sintering can be thought of as comprising three stages (De Jonghe and Rahaman, 2003). As described by De Jonghe and Rahaman (2003), necks form between particles and sintering begins in the initial stage. The necks are very concave in appearance at this point but this lessens during the intermediate stage where pores form continuous channels. In the final stage, further sintering disconnects the channels into individual separated pores.

In solid-state sintering, matter such as atoms and ions diffuse (Rahaman, 2007). The majority of material transport mechanisms that occur during sintering in crystalline materials are diffusion: surface diffusion; lattice diffusion from the surface and grain boundaries, and grain boundary diffusion (De Jonghe and Rahaman, 2003). The latter two, together with plastic flow, cause densification during sintering. Vapour transport does not cause densification, but instead causes material to transport to the necks (De Jonghe and Rahaman, 2003). Surface and lattice diffusions also cause neck growth (De Jonghe and Rahaman, 2003).

As was eluded to at the start of Chapter 2, the average particle size, particle size distribution, and morphology of an input powder can affect how the material sinters. A reduction in particle size increases the sintering rate, provided that densification

dominates, which allows lower sintering temperatures to be used (De Jonghe and Rahaman, 2003). A wide particle size distribution can allow higher densities to be achieved by improving the packing fraction. However, depending on whether the packing is homogeneous or heterogeneous, unwanted differential sintering (see Glossary) can occur (De Jonghe and Rahaman, 2003). Spherical particles enable good packing but other geometries will typically have lower packing densities and sintered density (De Jonghe and Rahaman, 2003). However, De Jonghe and Rahaman (2003) noted that other studies have found that high sintered densities with acicular shaped particles (see Glossary), which one assumes could include lath-shaped particles, can be achieved assuming alignment and homogeneous packing.

2.1. Spark Plasma Sintering (SPS)

Spark plasma sintering (SPS) is an alternative technique to conventional sintering methods e.g. cold-press-and-sinter or hot pressing. The SPS method has taken several decades to evolve to its current iteration (Tokita, 1999), which is now commercialised (Munir et al., 2006) with several companies making dedicated systems e.g. Franhoufer and FCT Systeme GmbH. Consequently, it is a popular technique, with over 7370 papers published in 2013 according to a Scopus database engine search result in July 2017.

Although SPS is extensively used, there is no consensus about the fundamental theory behind it (Aalund, 2009), despite the agreed benefits. The reason is that plasma has not yet been definitively observed during SPS (Munir et al., 2006, Saunders et al., 2015). The original and still fairly prevalent theory of the plasma's generation is that it is "a consequence of spark-discharge caused by high-energy, low-voltage, pulse DC current at high temperatures" (Aalund, 2009). "Even in a vacuum, on heat and pressure application, fine plasma can be produced as a consequence of the outgassing on particle surfaces" (Aalund, 2009). The typical SPS set-up is shown in Figure 3.1.

Other theories attribute consolidation of particles to Joule heating (Aalund, 2009), or Joule heating "except that the temperature is varied during the process by current pulse modulation" (O'Brien et al., 2009). The reader is referred to the article by O'Brien et al. (2009) for one possible description for the SPS process.

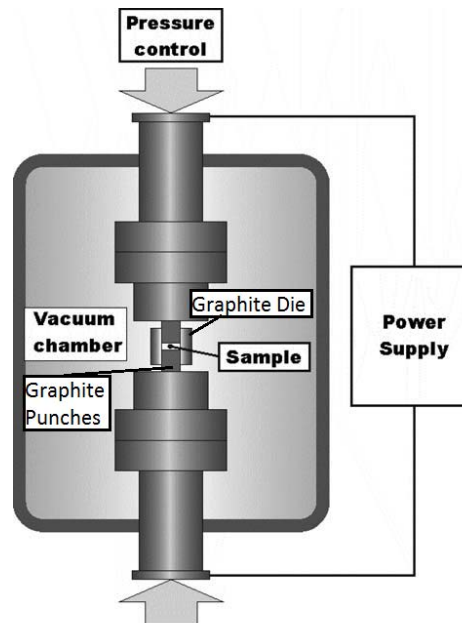


Figure 3.1: Schematic of the SPS process.⁹

2.2. Cold-Press-and-Sinter

This technique involves pressing a powder placed in a die under a predefined force (pressure) to pack the powder into a ‘green’ body. This body is then placed in a furnace and heated using the desired heating profile to sinter it. Typically, the green body is heated gradually up to a predefined temperature, held at that temperature for a defined duration and then cooled gradually again.

2.3. The ‘Pros and Cons’ of the Two Techniques

A detailed review of SPS conducted by Munir et al. (2006) highlighted that “current activated sintering, of which SPS is a form, can enable lower sintering temperatures to be used, shorter holding times and improvements of properties” (Munir et al., 2006), when compared to those made using conventional methods. Munir et al. (2006) have identified that there is an association between high densities and SPS, but that it is likely to be due

⁹ Journal of Materials Science, The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method, 41, 2006, 763, Z. A. Munir, U. Anselmi-Tamburini, M. Ohyanagi, (©2006 Springer Science + Business Media, Inc.) With permission of Springer.

to the use of smaller grain sized particles. Nevertheless it is difficult to distinguish the impact of grain size from that of the SPS process (Munir et al., 2006).

Orrù et al. (2009) conducted an extensive literature review comparing various electric current activated/assisted sintering techniques noting that SPS can enable near theoretical densities to be achieved in shorter time periods at lower sintering temperatures for nanometric powders. For the sintering of UO_2 , SPS has enabled sintering to be conducted in tens of minutes as opposed to hours (Ge et al., 2014).

The cold-press-and-sinter method has substantial heritage in the nuclear industry, which is a clear advantage over the use of a newer technique such as SPS. New techniques would require substantial initial capital investment, not just to build appropriate facilities but also to conduct risk assessments, which are essential to the safety-driven culture of this industry. The cost implications of high-throughput SPS for industry is being considered (Aalund, 2009). Spark plasma sintering requires a die to be present during sintering (see Glossary). A potential disadvantage of the technique over cold-press-and-sinter, which does not require a die, is that the die could react with the powder that is being sintered. SPS is advantageous in many applications as it requires no sample preparation and provides the potential to manufacture near-net shaped pellets (Ge et al., 2014). The definition of ‘near-net shape’ is provided in the Glossary.

3. Spark Plasma Sintering of Nuclear Fuels and their Surrogates

3.1. Uranium(IV) Oxide: UO_2

The literature showed that spark plasma sintering of UO_2 can enable pellets to be produced with relative densities greater than 95 % of theoretical density (T.D.) and with a somewhat wide flexibility in the SPS parameters. A review of three investigations is provided in this section followed by a description of the impact of sintering parameters on grain size and porosity in § 3.1.2 and an account of measured mechanical properties in § 3.1.3.

3.1.1. UO_2 SPS Procedures

Muta et al. (2013) investigated the SPS of $\text{Th}_{1-x}\text{U}_x\text{O}_2$ with different x-values, which were created by solid-state reactions using ThO_2 and $\text{UO}_{2.15}$. Only the UO_2 SPS pellets are considered in this review i.e. $\text{Th}_{1-x}\text{U}_x\text{O}_2$ with x equal to 1. The separate oxides were ball-milled (see Muta et al. (2013) for further details), cold pressed and then sintered at 1873 K

[~1600 °C] for 72 h in a 4 % hydrogen/argon gas environment (Muta et al., 2013). This sintering step was only conducted to allow a solid state reaction to create the $\text{Th}_{1-x}\text{U}_x\text{O}_2$ material, but it is assumed that the step was still conducted to make the UO_2 and ThO_2 spark plasma sintered material. After subsequent ball milling and packing into a graphite die, the powder was spark-plasma sintered at a specified temperature and at 50 MPa under flowing argon (Muta et al., 2013). An 80 K min^{-1} average heating rate and a 10 minute hold time were used, where samples were permitted to cool after this hold time (Muta et al., 2013). The total process lasted for 40 minutes (Muta et al., 2013). The pellets were reduced to UO_2 by heating in an argon, hydrogen and water vapour environment (Muta et al., 2013). Pure UO_2 pellets and ThO_2 pellets were also cold-pressed-and-sintered to allow a comparison between the SPS and conventional sintering of the materials. Cold pressing was carried out at pressures of 150 MPa and subsequently sintering parameters of 1873 K and 10 hour hold periods were applied. Sample density measurements allowed comparisons to be made between different sintering methods (Muta et al., 2013).

Muta et al. (2013) illustrated that for their procedures, SPS enabled the production of higher relative density pellets than conventionally sintered pellets. Their plotted data were inspected. From this it was estimated that the UO_2 SPS pellet had a density of around 95.5 % T.D. and the conventionally sintered pellet had a density of around 81.5 % T.D. (no quantitative uncertainties were given for either).

Ge et al. (2013) investigated the SPS of UO_2 with the objectives of minimising the maximum sintering temperature, minimising total sintering duration and producing pellets with 96 % theoretical density (T.D.). The effects of heating rate (200 °C min^{-1} and 100 °C min^{-1}), holding time (30 s, 5 minutes and 20 minutes), and applied pressure on density, densification, densification rate, grain size and inter-granular and intra-granular pores formation were assessed (Ge et al., 2013). They identified that conventional sintering of UO_2 took several hours (specifically between 2 and 8). Changing the specific surface area of the raw UO_2 material during the sintering process enabled the production of sintered UO_2 at lower temperatures (~1200 °C) (Ge et al., 2013). An alternative method for working at lower temperatures was to sinter hyperstoichiometric uranium oxide, UO_{2+x} , and to reduce it in hydrogen (Williams et al., 1959). Ge et al. (2013) provided further details on the conventional sintering of UO_2 and reported that densities greater than 96 % T.D. were achieved.

Ge et al. (2013) used $\text{UO}_{2.11}$ powder with mean particle (agglomerate) size of $2.4\text{ }\mu\text{m}$, and grain (crystallite) size between 100 and 400 nm. After SPS and the removal of graphite foil and aerosol (used as a lubricant and to provide a protective layer between the sintering die and the material of interest) from each pellet's surface, the pellets were reduced to form UO_2 using ASTM standard C1430-07 (Ge et al., 2013). The particle morphology of the reduced material was not characterised. The sintering temperatures were between $850\text{ }^\circ\text{C}$ and $1525\text{ }^\circ\text{C}$. The maximum temperature was held for the desired holding time. The applied pressure (applied for the hold time) was 40 MPa at the maximum hold temperature. This was in addition to the uncontrolled pressure, which was between 14 MPa and 24 MPa. The effect of the additional pressure on relative density was investigated. It was possible for the overall SPS process to take 10 minutes when shorter holding times of less than 10 minutes were used.

Ge et al. (2014) used the same SPS procedure as Ge et al (2013) to produce UO_2 pellets but instead used $\text{UO}_{2.16}$ as the hyperstoichiometric UO_2 material, and a heating rate of $200\text{ }^\circ\text{C min}^{-1}$.

For a high heating rate ($200\text{ }^\circ\text{C min}^{-1}$), a 30 s SPS hold time, no controlled pressure and a low sintering temperature of $850\text{ }^\circ\text{C}$, a relatively low UO_2 pellet density of around 78.4 % of T.D. was made by Ge et al. (2013). They were able to increase relative density to 86.5 % T.D. by applying the additional pressure, and keeping all other variables previously noted the same. They required an increase in temperature to further increase relative density. Temperatures of $1050\text{ }^\circ\text{C}$ and $1150\text{ }^\circ\text{C}$ were able to provide around 95 % of T.D. However, similar relative densities were also achieved by Ge et al. (2013) with the $100\text{ }^\circ\text{C min}^{-1}$ heating rate, and a longer hold time of 5 minutes at similar or higher temperatures.

Figure 3.2 illustrates some of their results for various heating rates, temperatures, and hold times, with and without (labelled) additional pressure. Ge et al. (2013) identified that the application of pressure had a greater effect on the density at lower sintering temperatures, than it did at high temperatures (see the $1500\text{ }^\circ\text{C}$ results in Figure 3.2). A better comparison would require pellets sintered at the same heating rate and for the same holding time to be compared at the two temperature extremes with and without controlled pressure. This would definitively determine whether the effect of heating rate has an impact on the relative density.

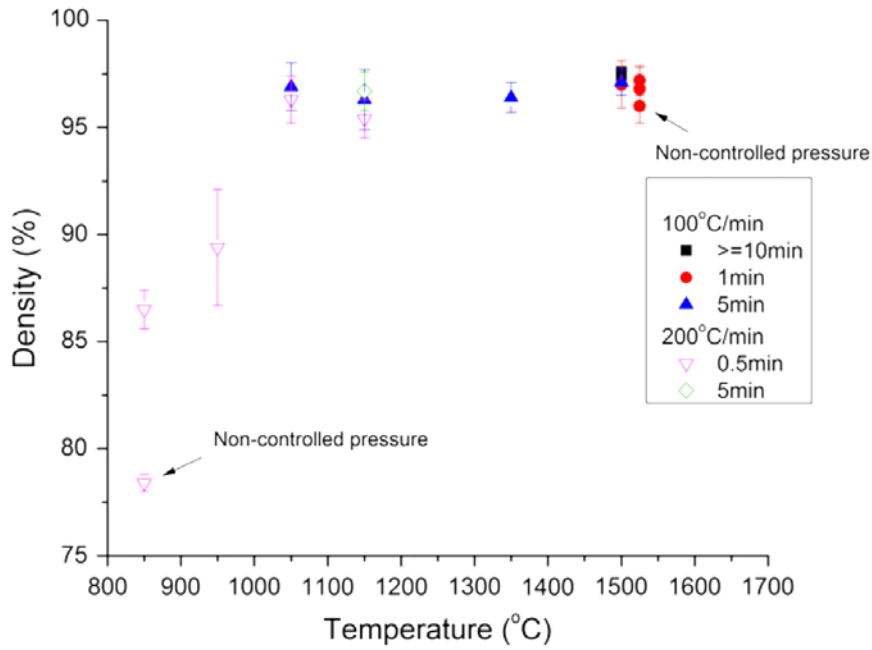


Figure 3.2: The variation of UO_2 pellet density with maximum sintering temperature, heating rate, hold time and application of controlled pressure measured by Ge et al. (2013).¹⁰

The combination of temperature and hold time may enable high relative density UO_2 SPS pellets to be created. Ge et al. (2014) found that the density of the UO_2 pellet could be controlled by either raising the maximum temperature or increasing the hold time. This was particularly true when below 95 % T.D. In other words, 95 % T.D. could be achieved using a hold time of 20 minutes (as opposed to 30 s) at a maximum heating temperature of 750 °C, but a 96 % T.D. could be achieved when a maximum temperature of 1050 °C was used for a 30 s hold time. This is illustrated in Figure 3.3. Above the 95 % T.D. level, further increases in hold time or temperature had little effect. Consequently densities did not exceed 98 % T.D. Hold time was thus found to have a greater influence if a low maximum SPS temperature was used.

¹⁰ Reprinted from the Journal of Nuclear Materials, 435/1-3, L. Ge, G. Subhash, R. H. Baney, J. S. Tulenko, E. McKenna, Densification of uranium dioxide fuel pellets prepared by spark plasma sintering (SPS), Pages 1-9, Copyright (2012), with permission from Elsevier.

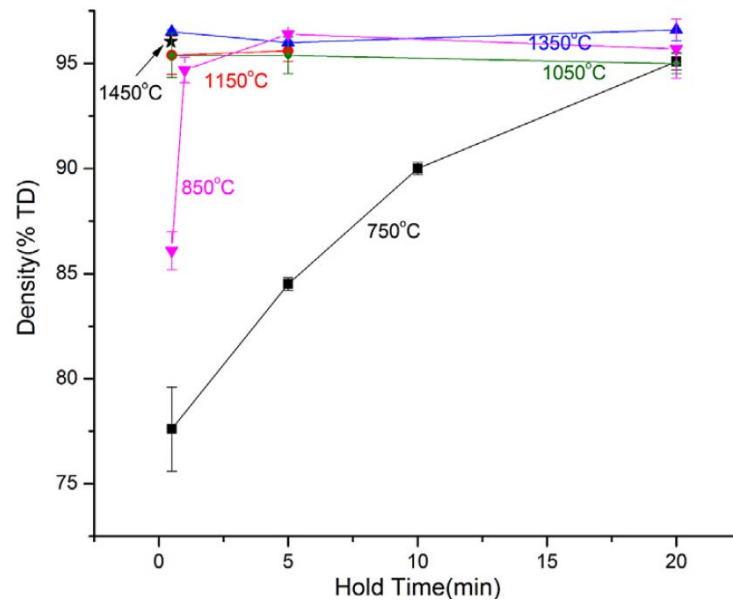


Figure 3.3: The variation of UO_2 pellet percentage of T.D. with hold time and maximum sintering temperature (Ge et al., 2014).¹¹

In conclusion, Ge et al. (2013) found that at least 96 % T.D. could be achieved with SPS and UO_2 provided that a maximum sintering temperature of at least 1050 °C and a hold time of at least 30 s was used in conjunction with an applied pressure of 40 MPa.

3.1.2. Grain Size and Porosity

Muta et al (2013) neither gave nor measured the grain size of their raw $\text{UO}_{2.15}$ material. Thus the effect of particle size on the conclusions of their investigation cannot be commented on. Muta et al. (2013) believed grain size to be unaffected by experimental SPS conditions. However, they attributed their larger hardness values, when compared to those in the literature, to small grains caused by the short duration of the spark plasma sintering process.

Ge et al. (2013) also investigated the effect of hold time on grain size. Scanning electron microscope (SEM) micrographs of a pellet sintered at 1150 °C were taken before and

¹¹ Reprinted from the Journal of the European Ceramic Society, 34/7, L. Ge, G. Subhash, R. H. Baney, J. S. Tulenko, Influence of processing parameters on thermal conductivity of uranium dioxide pellets prepared by spark plasma sintering, Pages 1791-1801, Copyright (2014), with permission from Elsevier.

after thermal etching (see Glossary) at 1400 °C for 30 minutes. From these, the average grain size was identified to be $2.9 \pm 0.3 \mu\text{m}$ (Ge et al., 2013). The conclusion was that the etching process had a small effect on grain size. They concluded that the grain growth during SPS (from the original $2.4 \mu\text{m}$ size) was due to a rapid heating rate and a short hold time. Large numbers of inter-granular and intra-granular pores were observed in the case of the pellet sintered for 5 minutes at 1150 °C. Ge et al. (2013) proposed that the heating rate and pressure applied along the ram direction at peak sintering temperature affected the inter-granular and intra-granular porosity of pellets and that necking between grains produced closed pores preventing gas from escaping. However, the inter-granular pores were more likely to diminish as a result of grain boundary diffusion during neck formation. An increase in heating rate corresponded to a decrease in inter-granular pores and an increase in intra-granular pores. The latter could potentially trap gas and increase thermal conductivity.

Ge et al. (2013) observed that an increase in hold time at a constant 1500 °C resulted in an increase in grain size. Ge et al. (2013) noted that density increased minimally with an increase in hold time in spite of an increase in grain size; however, on inspection of the stated values with their relative uncertainties ($97.0 \pm 1.1 \%$ T.D., $97.1 \pm 0.6 \%$ T.D. and $97.4 \pm 0.4 \%$ T.D. for 1 minute, 5 minute and 10 minute holding times respectively) no discernible difference can be noted.

If this test were to be conducted isothermally for different time periods and assuming CeO_2 behaves similarly to UO_2 under such conditions, then it is possible that holding time could impact CeO_2 grain growth during SPS. CeO_2 has been used as a surrogate for UO_2 (Miao et al., 2014). It is also unclear whether the effect of heating rate was tested for UO_2 or the sintered pellet before it had been reduced ($\text{UO}_{2.11}$). If it was the former, and if CeO_2 behaves similarly to UO_2 under such conditions, then it is possible that heating rate could have an impact on the porous nature of a CeO_2 pellet and prevent 100 % T.D. being reached, by producing intra-granular pores. As was suggested in the early ESA requirements for the ^{241}Am oxide RPS fuel pellets (see § 2.1 of Chapter 1), a current objective of the ESA programme is to allow the helium gas produced by ^{241}Am alpha decay to outgas through the pellet structure in order to avoid pellet swelling. Consequently, it is likely that intra-granular porosity will want to be minimised as it could potentially trap helium gas.

Ge et al. (2013) found UO_2 grain sizes to be affected by a change in holding time and maximum sintering temperature. At the lowest considered maximum SPS temperature of 750 °C, an increase in holding time only caused a small increase in grain size. However, at the lowest holding time of 30 s, an increase in maximum temperature caused a much larger increase in grain size. It appeared that grain size was maximised when Ge et al. (2014) used a 1350 °C maximum SPS temperature and a 30 s holding time; however, Figure 3.4 shows that within error, a 1450 °C maximum SPS temperature and 30 s holding time was also likely to maximise grain size.

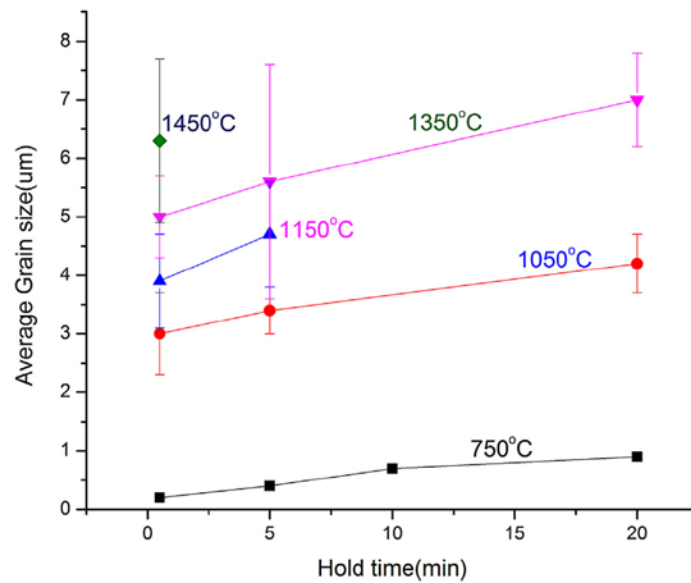


Figure 3.4: The variation of average grain size with hold time and maximum temperature Ge et al. (2014).¹¹

According to Ge et al. (2014), grain size depends on the T.D. of a pellet irrespective of the hold time or maximum SPS temperature. The results from Ge et al (2014), which show the variation of grain size with density, are illustrated in Figure 3.5.

Ge et al. (2014) noted that the grain size-density relationship and microstructure was comparable with those of other materials that were sintered conventionally and that the relationship was also comparable with that of alumina that had undergone SPS (Santanach et al., 2011).

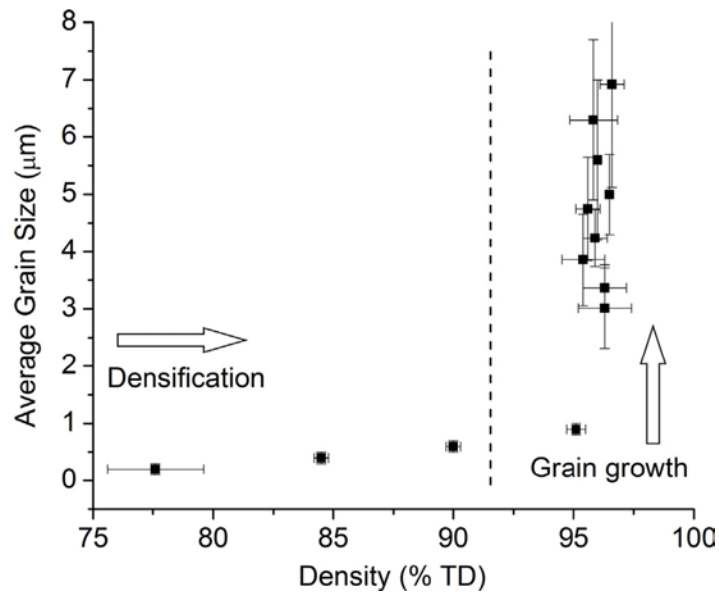


Figure 3.5: The variation of average grain size with percentage of theoretical density for the SPS of UO_2 (Ge et al., 2014).¹¹

The proposed explanation for this change in grain size with increased density is as follows: on densification, applied pressure improves grain proximity but inter-granular pores, which prevent grain boundaries from moving, limiting grain growth. However, an increase in temperature (when at high temperatures) enables grain boundaries to move, which results in pore size reduction, and thus an increase in density (Ge et al., 2014). Neck formation and growth between grains separated by inter-granular pores can result in intra-granular pores. The neck formation and growth also causes a corresponding increase in particle size. The remaining porosity is due to the short sintering time. A suggested approach would be to further increase the hold time, which could minimise the intra-granular porosity further, but the extent of this may be limited.

3.1.3. Mechanical Properties

Muta et al. (2013) spark plasma sintered $\text{UO}_{2.15}$ pellets, which they reduced to UO_2 form. They measured the Young's modulus and Vickers hardness of each of the pellets. They created a UO_2 pellet that was approximately 96 % T.D. (closer to 95.5 % T.D. but no error bars were provided) with approximate Young's modulus of 187 GPa. Vickers hardness was interpreted from a results graph (their Figure 7) to be around 6.4 ± 2.5 GPa and as a load of 9800 N (provided by a 1 kg mass) was used (for 15 s), it is assumed that the results are representative of the macro hardness of the material (The concept of macro

hardness is described in Chapter 4). Ge et al. (2013) measured a range of values for different grain sizes as shown in Figure 3.6.

Ge et al. (2013) mechanically tested their UO₂ pellets and found the average Vickers hardness varied linearly with the inverse square of the grain size (Ge et al., 2013). The results are shown in Figure 3.6. However, as loads provided by 200 g, 500 g and 1 kg masses were used for the Vickers hardness indentation tests, the link between the results and bulk material properties is unclear.

Young's modulus and Poisson's ratio were also found. The former was determined using ultrasonic techniques, and increased with relative density (Ge et al., 2013). On visual comparison, the values were in reasonable agreement with those in the literature. Ideally, a statistical test should be conducted with a null hypothesis that the two data sets are dissimilar e.g. a Student's T-test.

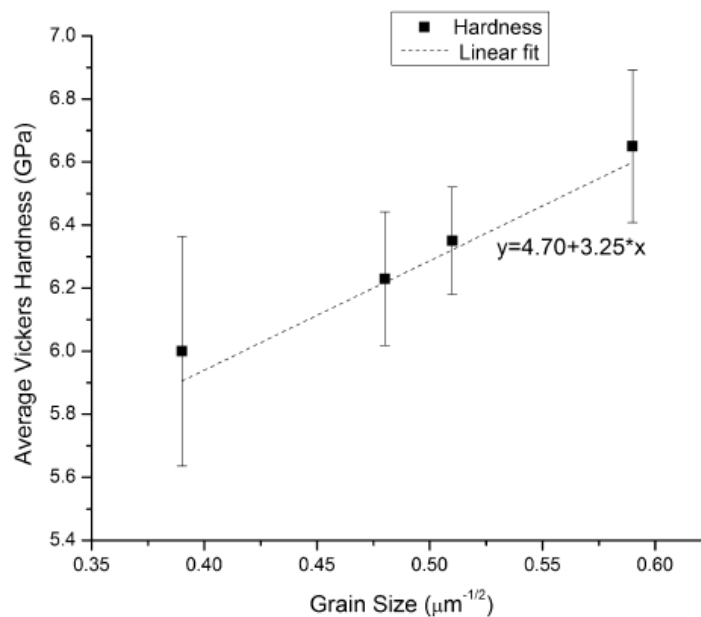


Figure 3.6: The variation of average (micro) Vickers hardness with grain size for three different loads (provided by 200 g, 500 g and 1 kg masses) measured by Ge et al. (2013).¹⁰

Ge et al. (2013) results of the variation of Young's modulus with relative density include a best fit but with no drawn error bars. On visual inspection, the pellet with 96 % T.D. would have a Young's modulus of around 197 GPa, but the error could not be estimated. Ge et al (2013) note that pellets with greater than 95 % T.D. were found to have an average Young's modulus of 204 ± 18 GPa. The UO_2 SPS pellets' Young's modulus results of Ge et al. (2013) and Muta et al. (2013) are thus consistent. Ge et al. (2013) compared their results with those of UO_2 in the literature (The reader is referred to Ge et al. (2013) for further details.) and appeared to show consistency. It can only be assumed that the pellets noted in the literature were sintered conventionally. Muta et al. (2013) found that their spark plasma sintered UO_2 pellet had a lower Young's modulus when compared to those of other studies which produced pellets with different densities.

Hagman and Reymann (1979) produced a semi-empirical model to describe the variation of Young's modulus of UO_2 with porosity (density) and temperature. They considered numerous data from many sources, and it appears that at room temperature, for a density of ~ 96 % T.D., a large range of Young's modulus experimental data exist (for UO_2 above 450 K), with two points at 215 GPa or 200 GPa.

3.2. CeO_2 as a Surrogate for $\text{UO}_2/\text{PuO}_2/\text{NpO}_2$

Choi et al. (2010) investigated the SPS of nanometric (see Glossary) CeO_2 as a surrogate for nuclear oxides. They conducted a subsequent investigation to understand the SPS behaviour of nanometric-grained Dy_2O_3 doped CeO_2 (Choi et al., 2012). The latter also included SPS work of pure ceria, which will be the content discussed in this chapter. These studies by Choi et al. were the only two known investigations to have studied the SPS of pure ceria (Choi et al., 2010, Choi et al., 2012) before the sintering study of this thesis (presented in Chapter 6) had begun.

Choi et al. (2010) examined the effect of temperature (between 650 °C and 780 °C); pressure (400 MPa and 700 MPa); heating rate (between 90 °C min⁻¹ and 330 °C min⁻¹) and holding time (from 0 to 10 min) on the relative density of SPS sintered pellets and their effect on grain size. The commercially sourced material comprised particles around 25 nm in size. They created a specially made die to enable the (5 mm diameter sample with a thickness of 1.5 mm) pellets to be subjected to large pressures while maintaining the ability to heat at fast rates. Prior to heating, the samples in the die were pressed at

150 MPa. The pressure was increased from the onset and reached its maximum value at the final sintering temperature (Choi et al., 2010).

Choi et al. (2010) created CeO₂ pellets with at least 98 % T.D., using a heating rate of 130 °C min⁻¹, 500 MPa of pressure, and a 5 minute hold time at temperatures of 650 °C or higher. Temperature was found to have a small impact on relative density. Uncertainty values were not reported. They used a lower temperature than Zhou and Rahaman (1997), who sintered similar sized CeO₂ at 1150 °C using the cold-press-and-sinter method and achieved around 95 % T.D (see § 4.2 for more details). Choi et al. (2010) analysed their SEM images and found that an increase in temperature resulted in a grain size increase from ~27 nm to 55 nm. However, grain size estimation from crystallite size by XRD pattern analysis indicated a less significant size increase (from 25 nm to 34 nm).

An isothermal increase in pressure caused an increase in relative density, with the greatest increase between 400 MPa and 500 MPa for the same heating rate and holding time previously noted. However, all densities were above 93 % T.D. It was difficult to determine whether grain sizes in the final pellet were affected by an increase in pressure. In the case of no hold time and a 780 °C sintering temperature, they found that an increase in heating rate from 90 °C min⁻¹ to 330 °C min⁻¹ resulted in an increase in relative density, but also resulted in a reduction of grain size but only slightly from 113 nm to 88 nm (Choi et al., 2010).

Choi et al. (2012) used a similar SPS procedure as Choi et al. (2010) to sinter CeO₂ with a larger particle size of 133 nm using a larger temperature range of 800 °C to 1100 °C and heating rates from 130 °C min⁻¹ to 300 °C min⁻¹. They found the relative density increased with temperature e.g. from around 81.5 % T.D. at 990 °C (for 500 MPa, 130 °C min⁻¹ and 5 min holding time) to around 91 % T.D. at 1050 °C. In their 2010 investigation, Choi et al. (2010) sintered the CeO₂ to around 98 % T.D. using sintering temperatures between 650 °C and 700 °C (densities slightly increased with temperature) for the same pressure, heating rate and holding time as their 2012 investigation. However, this earlier investigation used smaller CeO₂ particles (Choi et al., 2010). It is likely that the initial particle size of the CeO₂ impacts the relative densities that can be achieved.

Choi et al. (2012) also found relative density to increase with an increase in applied pressure, but the grain size within the sintered material to not be significantly affected by an increase in pressure. This was shown in their SEM images (Choi et al., 2012). Relative densities were found to increase with holding time but then plateaued. Apart from a difference in the effect of heating rate on relative density, Choi et al. (2010) and Choi et al. (2012) found the effect of pressure, temperature and holding time on relative density and grain size to be very similar even though they used nanometric particles whose sizes differed by an order of magnitude and used variables in sintering conditions with different ranges.

Roleček et al. (2017) spark plasma sintered milled CeO_2 at 1300 °C using a 50 MPa pressure for 5 minutes to achieve a pellet density of 92.7 % T.D . They did not report the particle size and morphology of the powder, (specifically whether the particles were lath-shaped). Their XRD data suggested CeO_2 had reduced to Ce_2O_3 . The study by Roleček et al. (2017) was a comparative study that compared the SPS and cold-press-and-sinter of CeO_2 (see § 4.2).

3.3. Benefits and the foreseen challenges in the SPS of CeO_2

The SPS work of this study (see Chapter 6) was conducted in collaboration with Queen Mary University of London. Discussions prior to starting these investigations highlighted that there could be difficulties in the SPS of CeO_2 based on their previous experience. A literature review was conducted to establish the research community's state of knowledge about this topic. As Choi et al. (2010) and Choi et al. (2012) were the only known teams exploring the SPS of pure CeO_2 (when the sintering study of this thesis began) and as they did not identify any benefits or problems, the literature review was expanded to consider the behaviour of CeO_2 when sintered conventionally at lower temperatures or in reducing environments. This was because these environments are typically associated with SPS.

However, there has been no known research into the SPS of pure micrometric CeO_2 . Therefore key points from the literature on conventionally sintered nanometric CeO_2 (Ozawa, 2004, Chen and Chen, 1995) and spark plasma sintered nanometric CeO_2 (Choi et al., 2010, Choi et al., 2012) have been noted in order to hypothesise possible benefits or difficulties associated with the SPS of CeO_2 . Literature that addressed Ce behaviour at

low temperature and in reducing environments are considered as these are associated with SPS and are thus more appropriate.

3.3.1. Potential Benefits

Ozawa (2004) investigated the (conventional) sintering of two separate samples of size 14 nm (powder A) and 60 nm (powder B), respectively, with an increase in temperature in air. They measured the variation of the weight loss of each powder with an increase in temperature. Their results are shown in Figure 3.7. The relative density variation with temperature increase for both samples showed an inflection around 1600 °C, which they associated with oxygen outgassing (Ozawa, 2004) by comparing the result with those of Zhou and Rahaman (1997). Additionally, Ozawa (2004) observed increased densification rates above 1600 °C.

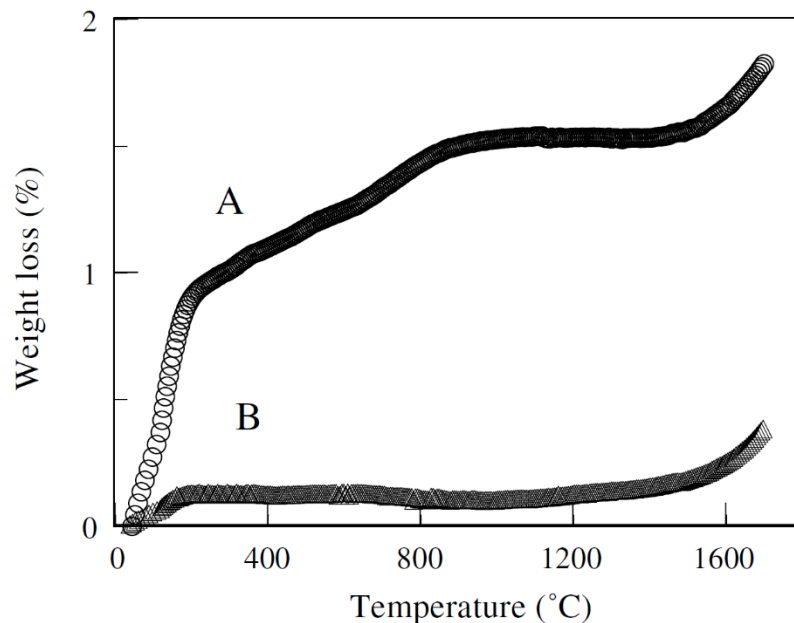


Figure 3.7: The measured weight loss of powders A and B with an increase in sintering temperature. A 5 °C min⁻¹ heating rate was used.¹²

¹² Reprinted from Scripta Materialia, 50/1, M. Ozawa, Effect of oxygen release on the sintering of fine CeO₂ powder at low temperature, p. 61-64, Copyright (2004), with permission from Elsevier.

Powder A also exhibited a weight loss when heated between 700 °C and 800 °C, which was associated with oxygen outgassing (Ozawa, 2004). Meanwhile they observed an increased densification rate in this temperature range. Ozawa (2004) noted that this lower temperature weight loss is a “novel character of fine CeO₂ on sintering”; it was not observed for the coarser, yet still nanometric, powder B. They also briefly remarked that there is some literature in the automotive exhaust catalyst field¹³ that has observed the oxygen release of CeO₂ between 400 °C and 1000 °C. As well as the weight loss that indicated the reduction of CeO₂, Ozawa (2004) found that the XRD pattern of a sample sintered at 1500 °C (with broad peaks) was cubic and evidenced peak shifts when compared to a sample sintered at 1400 °C (Ozawa, 2004). This suggested a CeO_{2-x} structure¹⁴ was produced at the higher temperature (Ozawa, 2004). They did not provide the XRD patterns.

Ozawa (2004) found evidence of pores in material heated at 1700 °C, and so expected oxygen outgassing to inhibit densification. Yet, they suggested that the reduction of CeO₂ during sintering in an air environment above 1500 °C could aid densification (Ozawa, 2004), as it causes oxygen to move in the material and enhance the bulk diffusion in the nonstoichiometric CeO_{2-x} lattice. Their results showed that relative density increased with temperature, and densification rate increased above 1600 °C.

3.3.2. Potential Difficulties

Although there were few published studies in the literature on the SPS of CeO₂, the topic was being actively researched in the USA and Finland according to a ResearchGate discussion forum (ResearchGate Discussion, 2013-2014). In the forum, researchers discussed the difficulty with sintered body cracking when spark plasma sintering CeO₂. Differences in the thermal expansion coefficients of graphite (the die) and ceria was mentioned (ResearchGate Discussion, 2013-2014). Others noted cracking parallel to the compression direction. Another observation was that the sintered ceria exhibited colour layering and a proposed possible cause for this was the incomplete reduction of CeO₂ (ResearchGate Discussion, 2013-2014). However, despite the discussion, no conclusive

¹³ The use of nanometric powders is prevalent in this field of research.

¹⁴ In this thesis, the substoichiometric CeO₂ has been described as CeO_{2-(x/2)}. CeO_{2-x} is the more common term.

reasoning for the cracking problem was provided. Although care must be taken when referring to unpublished literature, the arguments suggested by the researchers were reasonable for consideration.

A thorough investigation of the different phases between $\text{CeO}_{1.5}$ and CeO_2 was conducted by Bevan (1955), who recorded the colours of the different phases produced under different annealing conditions. In the context of this thesis, it was decided that colour observations of the spark plasma sintered ceria sintered in this study would be relevant and would provide a litmus paper-type test for the reduction of the sintered samples (see Chapter 6).

Mori et al. (2005) and Mori and Drennan (2006) identified difficulties in the densification of doped nano- CeO_2 electrolytes caused by the reaction with the carbon in the graphite die, which was believed to lower the bulk density (Mori et al., 2005) as well as the sensitivity of CeO_2 to reduction. In order to minimise reaction with the carbon-based die a zero holding time at the sintering temperature was used. This was done by immediately switching off the current and releasing the pressure at the end of the sintering process.

Zhou and Rahaman (1997) measured the weight loss of sub-micrometric CeO_2 during thermal treatment (see § 3.3.1 for more details) and suggested the following described by Meriani (1989) to be the cause: CeO_2 is reduced to Ce_2O_3 when sintered above 1200 °C. The evolved associated oxygen gas results in pore production, and the amount evolved reduces with CeO_2 particle size (Zhou and Rahaman, 1997). Full density can be achieved at higher temperatures.

3.3.3. Reduction Conditions for CeO_2

For completeness, it is noted that the reduction of CeO_2 under different oxygen partial pressures and temperatures has been investigated in the literature e.g. by Bevan and Kordis (1964), as is illustrated in Figure 3.8.

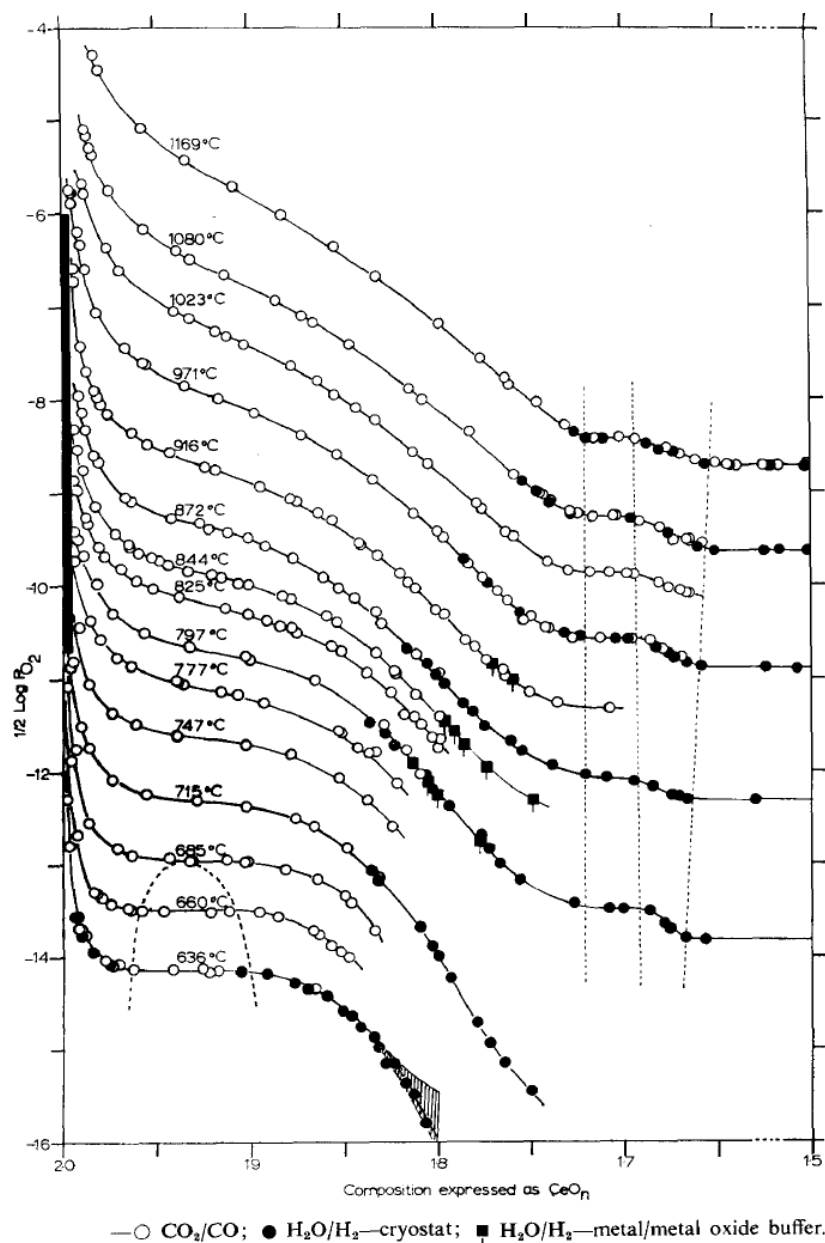


Figure 3.8: A graph illustrating the effect of oxygen partial pressure on CeO_n composition where n is between 0 and 1, inclusive. The data were recorded by Bevan and Kordis (1964).¹⁵

¹⁵ Reprinted from the Journal of Inorganic Nuclear Chemistry, 26, D. J. M. Bevan and J. Kordis, Mixed Oxides of the Type MO_2 (Fluorite)- M_2O_3 -I Oxygen Dissociation Pressures and Phase Relationships in the System CeO_2 - Ce_2O_3 at High Temperatures, Pages 1509-1523, Copyright (1963), with permission from Elsevier.

4. Cold-Pressing-and-Sintering of Nuclear Fuels and their Surrogates

4.1. Americium Oxides

Few americium oxide sintering studies have been conducted to date (Sari et al., 1970, Sari and Zamorani, 1970, Casalta et al., 1995, Nishi et al., 2008).

Sari and Zamorani (1970) conducted an investigation to help establish the Am-O phase diagram by creating $\text{AmO}_{2-(x/2)}$ with a range of fractional x-values. In doing so they fabricated 90 % T.D. AmO_2 pellets by the cold-press-and-sinter method in air using a 1600 °C sintering temperature. It is noted that the isotope of americium was not stated in either of their investigations (Sari and Zamorani, 1970, Sari et al., 1970). Further details of how the substoichiometric pellets were created can be found in the paper by Sari and Zamorani (1970), but essentially it involved heating the pellets to different temperatures in different gaseous atmospheres to reduce them. Although they illustrated and described the microstructures of the $\text{AmO}_{2-(x/2)}$, they did not comment on the AmO_2 pellets. As an aside, samples with two different $\text{AmO}_{2-(x/2)}$ phases not only evidenced this in X-ray diffraction data but also in the microstructure.

Another report by Sari et al. (1970) that focused on the ceramography of $\text{AmO}_{2-(x/2)}$ pellets made using a very similar, if not the same, sintering method illustrated the microstructure of the AmO_2 pellet cooled gradually from 1400 °C. This is illustrated in Figure 3.9. The figure evidenced pores with an even spread.

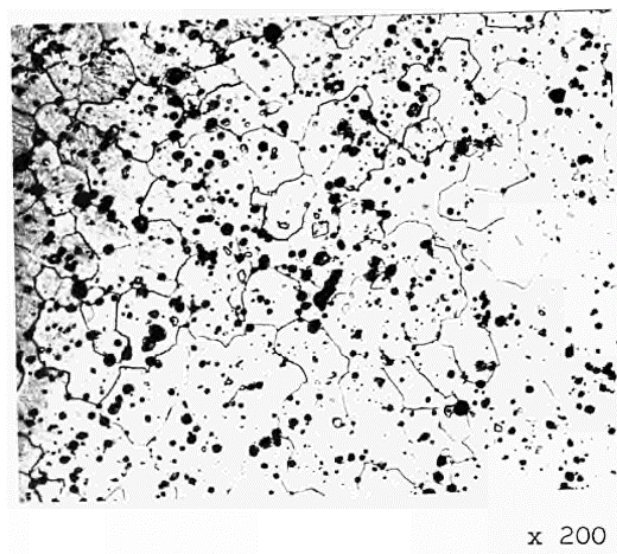


Figure 3.9: The microstructure of AmO_2 cooled gradually from 1400 °C. The sample was “vacuum cathodic etched” (Sari et al., 1970).¹⁶

Casalta et al. (1995) conducted an investigation to collect experimental data to contribute towards the populating and understanding of the Am-O phase diagram. They mixed $^{241}\text{AmO}_2$ and binder and pressed the material to form green pellets. A dilatometer was used to sinter the pellets to 85-90 % T.D. using a maximum sintering temperature of 1500 °C (Casalta et al., 1995). However, they did not state what force was used to press the powder nor did they provide details of the particle properties of the initial powder. The binder was organic zinc stearate. The heating and cooling rates were varied to give the different relative densities but the values were not reported. Some of the pellets were then exposed to different gaseous environments to create various $\text{AmO}_{2-(x/2)}$ phases. Although they reported that ceramography was conducted, they did not provide or describe any results.

Nishi et al. (2011) created $^{243}\text{AmO}_2$ and $^{243}\text{Am}_2\text{O}_3$ pellets with densities of 85.6 % T.D. and 91.2 % T.D., respectively, for thermal conductivity and heat capacity investigations.

¹⁶ Permission to reuse this image (© European Union, 1995 – 2017) was received. It was required that the source be acknowledged in a specific way. This is provided at the end of this chapter.

The powder for each pellet was hand ground using an agate mortar. They did not state the pressure to press the green pellets. The AmO₂ green disc was sintered in flowing air (500 ml min⁻¹) for 6.5 hours at 1460 °C, and then heated for 3 hours at 800 °C. The Am₂O₃ disc was sintered in a N₂ + 4 % H₂ flowing (500 ml min⁻¹) atmosphere at 1460 °C for 5 hours.

4.1.1. Limited Hardness Data

Sari et al. (1970) measured the Vickers microhardness of their pellets and found AmO_{2.00} to have a hardness ranging from 6.47 GPa to 7.26 GPa. The values decreased with a reduction in x-value. They stated that the high porosity meant the results were not precise and that AmO_{2.00} had a Vickers hardness that was comparable to PuO_{2.00} (Sari et al., 1970). Unfortunately, they did not quote the force nor the duration of their Vickers indentations to allow ready comparison with other data in the literature (see Chapter 4). It is assumed that as they used a Vickers microhardness machine, loads less than those equivalent to a 1 kg mass were used. The exact loads used to measure the data were not provided. A similar trend of the reduction of Vickers hardness with a reduction in O to Am ratio (an increase in x) was found by Casalta (1996). The AmO₂ pellet had a Vickers hardness of around 6.9 GPa.

4.2. Cerium(IV) Oxide: CeO₂

Cerium(IV) oxide i.e. CeO₂, is used as a surrogate for UO₂ and PuO₂. In addition, the cold-press-and-sinter technique has extensive heritage. With both of these points in mind, it is beyond the scope of this review to assess all sintering studies on CeO₂. In § 2, it was noted that particle size, size distribution and shape impact the packing and sintering of the material. The reviewed literature on the cold-pressing-and-sintering of CeO₂ used nanometric or sub-micrometric material. No literature using lath-shaped material could be found. With this in mind, a brief literature review is provided, which describes the range of densities achieved and some mechanical properties of cold-pressed-and-sintered CeO₂.

Several studies report the ability to sinter CeO₂ to near-full density i.e. > 95 % of the theoretical density (Li et al., 2001, Zhou and Rahaman, 1993, Jahromi, 2009, Wang, 2006).

Roleček et al. (2017) cold-press-and-sintered milled and non-milled CeO_2 powder. It was noted in § 3.2 that Roleček provided no further information on particle characteristics. Green pellets (12 mm in diameter and 10 mm in height) were uniaxially pressed under a 50 MPa pressure. They were isostatically cold-pressed under 300 MPa for 1 minute. Pellets were sintered between 1300 °C and 1700 °C for 1 hour. Each sintering profile had a heating and cooling rate of 5 °C min⁻¹ and 10 °C min⁻¹, respectively. The sintered relative densities were 72.2 % T.D. to 91.3 % T.D. when non-milled powder was used and 81.4 % T.D. to 95.4 % T.D. when milled powder was used (the lower and upper relative densities corresponded to 1300 °C and 1700 °C sintering temperatures).

Wang (2006) cold-pressed ball-milled CeO_2 (originally 5 µm) into different geometries for use in different mechanical tests. They were ball milled with a binder. The green bodies were pressed using a two stage process: for 4 minutes under an initial uniaxial 35 MPa pressure and then isostatically for 5 minutes under a 250 MPa pressure. Discs ranging from around 0.95 cm to around 3.18 cm in diameter were fabricated and rectangular bars 1 cm long by 0.6 cm wide were also fabricated. The samples were heated to 400 °C to allow the binder to “burn out” for an hour and then sintered for 20 hours at 1550 °C. Wang (2006) used 5 °C min⁻¹ heating and cooling rates. Relative densities of at least 94 % T.D. were achieved. A four point bend test was used to determine flexural strengths of CeO_2 and of partially reduced CeO_2 samples, specifically, $\text{CeO}_{1.825}$, $\text{CeO}_{1.877}$ and $\text{CeO}_{1.991}$. Wang (2006) compared the flexural strengths and found that the “flexural strength was reduced significantly as a result of the reduction process”. They attributed it to microcracks that resulted when the samples were heated in reducing conditions, which made the fracture more likely. The CeO_2 sample had a strength of 127 ± 30 MPa but the $\text{CeO}_{1.877}$ had a strength of only 8 MPa (Wang, 2006).

Zhou and Rahaman (1993) sintered three different batches of CeO_2 . Each had different average particle size, specifically of around 14 nm (ultra-fine), 100-200 nm (precipitated) and 500 nm (0.5 µm; commercial). The latter was commercial material and the former two were created using different techniques; the reader is referred to their paper for further details. Discs (6 mm diameter and 3 mm thickness) were pressed under 50 MPa, then sintered in a dilatometer. Two sintering regimes were used: isothermal heating at around 1150 °C for two hours or under constant heating rates of 1 to 10 °C min⁻¹ up to 1400 °C. The former created discs with densities of 98 % T. D. using the 14 nm material.

Figure 3.10 shows that this material sintered to around 95 % T.D. at around 1200 °C when a constant heating rate of 5 °C min⁻¹ in air was used, but much higher temperatures were required to sinter the batches of larger particles to similar densities. Another way of interpreting this plot is that lower relative densities can be targeted by simply changing the temperature to which you sinter.

Zhou and Rahaman (1997) reported a very similar (if not the same) relative density against temperature plot in a later study where they attributed the points of inflection in Figure 3.10 to CeO₂ reduction to Ce₂O₃, which occurred at high temperatures. They explained that the sintered bodies made with larger particles (100-200 nm and 500 nm) had much lower relative densities when they outgassed oxygen, specifically, 80 % T.D. and 70 % T.D, than the sintered compact made with the 14 nm material. They stated that this was the reason for why the compacts sintered with the larger particles did not crack. Zhou and Rahaman (1997) stated that the oxygen travelled through the pore channels at these densities.

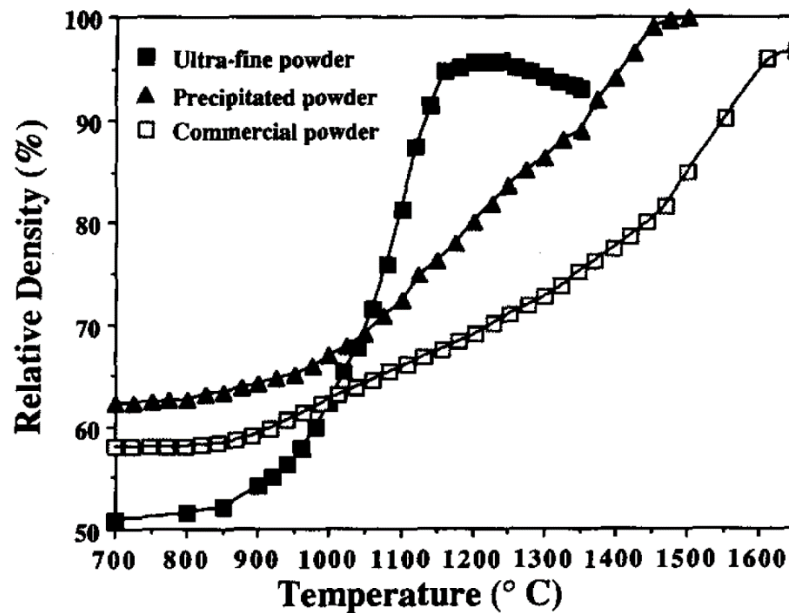


Figure 3.10: Illustrates the variation of relative density of sintered CeO_2 with temperature for different sized input powders: 14 nm (ultra-fine), 100-200 nm (precipitated) and 500 nm (0.5 μm ; commercial).¹⁷

Jahromi (2009) sintered sub-micron (average diameter of 0.38 μm) commercial CeO_2 material. Green pellets that were 1 cm in diameter and 0.35 cm thick (pressed to 57 % T.D. at 255 MPa) were heated at 5 $^{\circ}\text{C min}^{-1}$, and were sintered isothermally at different temperatures and for different specified holding times (two to fourteen hours). They cooled their samples by switching off the furnace. They were able to sinter samples with a range of relative densities even for 2 hour holding times e.g. those sintered at 1250 $^{\circ}\text{C}$ had 76.00 % T.D. and those sintered at 1550 $^{\circ}\text{C}$ had 98.60 % T.D.

¹⁷ Reprinted from Acta Materialia, 45/9, Y. Zhou and M. N. Rahaman, Effect of Redox Reaction on the Sintering Behavior of Cerium Oxide, Pages 3635-3639, Copyright (1997), with permission from Elsevier.

4.2.1. Hardness Properties

Jahromi (2009) measured the Vickers hardness of the sintered material using a 0.25 N load applied for 5 s. Samples sintered at 1700 °C for 0 hours with around 98 % T.D. had a hardness of 7.7 GPa. Lowering the sintering temperature to 1550 °C resulted in lower hardness values i.e. 5.3 GPa, 5.2 GPa and 4.6 GPa for 0, 8 and 14 hours of sintering (with similar densities of around 96, 98 and 98 % T.D. each).

4.3. Neodymium (III) oxide: Nd₂O₃

One of the few published Nd₂O₃ cold-press-and-sinter investigations was by Heintz et al. (1989). Their powder comprised particles with an average grain size of 4 µm and specific surface area of 1.8 m² g⁻¹. Their cubic compacts with a 7 mm dimension were uniaxially pressed at 300 MPa. A dilatometer was used to sinter the samples at 1440 °C for 10 minutes (Heintz et al., 1989). They investigated the impact of using air, nitrogen and argon environments on the sintered density. Their powders contained hydroxide (assumed to be from a hygroscopic reaction). When these powders sintered, the pellets cracked. The pellets had relative densities of between 86 and 89 % T.D. (Heintz et al., 1989). However, calcined powder sintered to around 91 % T.D. in air and argon environments and although they did not elaborate, they suggested the inert environments were favourable (no water). Heintz et al. (1989) sintered pellets to higher densities by using ground powder.

4.4. Lath-shaped PuO₂

The ESA americium oxide chemical flow sheet creates lath-shaped particles. As was mentioned in § 2, average particle size, particle size distribution, and morphology can impact sinterability. However, none of the sintering investigations reviewed thus far have used lath-shaped material. In order to gain an initial understanding of how lath-shaped material may sinter, some key points from a PuO₂ sintering investigation by Bickford et al. (1976) are provided. Their study involved comparing the cold-pressing-and-sintering and hot pressing of lath-shaped material, but only the former is reviewed here.

Bickford et al. (1976) created PuO₂ and cold-pressed-and-sintered it according to the conditions outlined in Table 3.1, which is reprinted from their paper. Sixteen batches of precipitated oxalate were used. Thus it is assumed that the particle properties of each differed. Only some of the outgassed material was ball-milled (in argon for 8 hours). The results are reprinted in Figure 3.11.

They stated that the desired density, e.g. 82 % T.D., was achieved using the processed powder, which is assumed to mean the ball-milled powder. The data appears to be omitted from Figure 3.11. Bickford et al. (1976) stated that the “fabricated dimensions are difficult to control.” They sintered pellets at a lower temperature initially to try and maintain the microstructure at the higher sintering temperature and prevent shrinkage. Bickford et al. (1976) stated that the pellets sintered using milled and non-milled powder were not “sufficiently stable nor reproducible to meet dimensional requirements”.

Table 3.1: The cold-press-and-sinter method (and hot-pressing method) used to fabricate PuO₂ pellets by Bickford et al. (1976).¹⁸

Table 1. Process for Fabricating PuO₂ Pellets

1) Precipitate plutonium oxalate 2) Calcine to PuO₂ (2 hr at 735°C in air) 3) Simulate ¹⁶O₂ enrichment (8 hr at 700°C in air) 4) Outgas (1 hr at 1000°C in air)	
Cold-Pressed Pellets	Hot-Pressed Pellets
5) Ball mill (8 hr in air) ^a	5) Ball or vibratory mill (varying periods in argon)
6) Cold press (58,000 psi, without binder)	6) Cold press (58,000 psi, without binder)
7) Sinter (3 hr at selected temperatures)	7) Crush (<125 μ)
	8) Presinter (3 hr at selected temperatures)
	9) Hot press (0.33 hr at 1530°C in graphite dies)
	10) Heat treat (12 hr at 1440°C in air)

^aStep omitted for some pellets.

¹⁸ In accordance with reuse guidance, the following information is provided: the research conducted by Bickford et al. (1976) at Savannah River Laboratory (as it was known as then) was prepared under a U. S. Energy Research and Development Administration contract, namely, AT(07-2)-1.

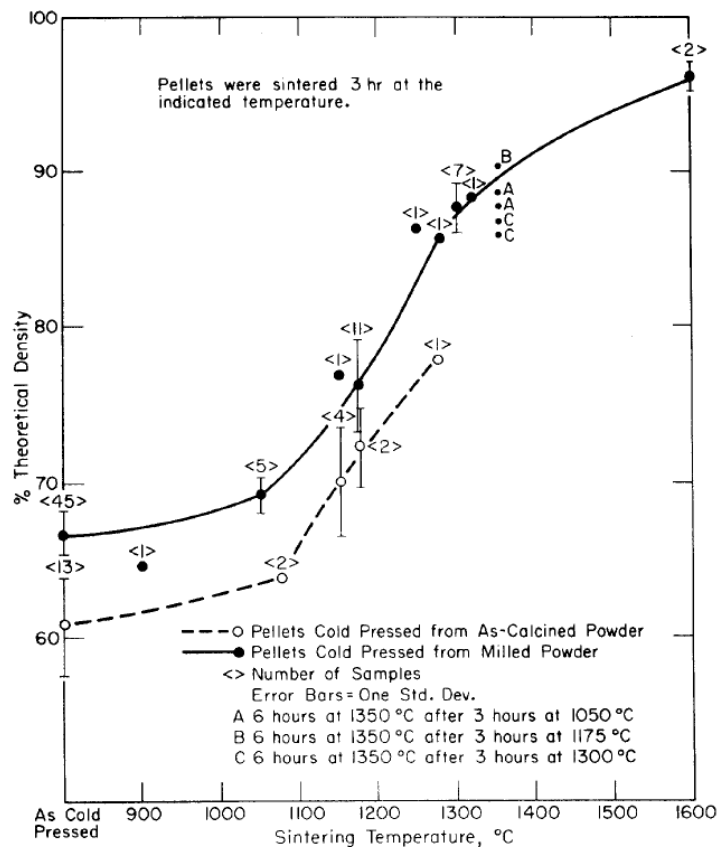


Figure 3.11: The effect of sintering temperature on the relative densities of cold-pressed PuO_2 (Bickford et al., 1976).¹⁸

5. Context for this Doctorate

A brief summary of some of the key trends of the studies outlined in § 3 and § 4 are provided in Appendix B.

It was stated in § 2.1 of Chapter 1 that an early requirement of the sintered fuel is to have a relative density that is between around 85 and 90 % T. D. to allow helium to outgas through the sintered body. Additionally, although not the focus of this thesis, it was noted that future fuel research will need to establish the requirements of the pellet microstructure and porosity as $^{238}\text{PuO}_2$ literature suggests that this was key to controlling He outgassing in GPHS and LWRHU pellets (McDonnell, 1978, Peterson, 1984). Pellet swelling will need to be avoided so as to not degrade cladding performance, particularly in accident scenarios. Therefore these relative density, microstructure and porosity requirements will be essential to the safety of ESA americium-based RPSs and their design with respect to accident scenarios.

The cold-press-and-sinter technique is a well-established method for sintering nuclear materials. This literature review has highlighted that the spark plasma sintering technique has been used to sinter nuclear fuels, namely UO_2 . It is capable of controlling the relative density, grain size, inter-granular and intra-granular porosity of a sintered compact by varying the parameters of the sintering process. Reducing the latter in future sintered Am oxide pellets may be important to minimising helium trapping.

There have been very few studies on the SPS of CeO_2 . The majority of these used nanometric material (Choi et al., 2010, Choi et al., 2012) and the study by Roleček et al. (2017) did not state the size nor morphology of the particles of their CeO_2 powder. Therefore there have been no known studies on the SPS of micrometric nor micrometric lath-shaped CeO_2 . Additionally, no public studies on the cold-press-and-sinter of lath-shaped CeO_2 were located. There have been no sintering investigations on the SPS of Nd_2O_3 . Thus the sintering study presented in Chapter 6 contributes to wider body of knowledge in the literature as well as the ESA programme. There are also few publicly published studies on the cold-press-and-sinter of Nd_2O_3 . Heintz et al. (1989) found that Nd_2O_3 powder cracked and suggested that environments that did not contain water were preferable for sintering Nd_2O_3 .

The review has identified that spark plasma sintering CeO_2 can result in cracked sintered bodies, but the cause for this has not been reported. Some sintering studies have observed material outgassing to occur when sintering CeO_2 (Ozawa, 2004, Mori et al., 2005, Zhou and Rahaman, 1997) and have attributed this to its reduction. Spark plasma sintering with graphite dies provides a reducing environment. Thus from this review, it is not unexpected that CeO_2 will reduce during the SPS investigations of this study (see Chapter 6). Colour observations could provide a litmus-paper type test for testing this hypothesis. Sintering temperature, hold time and pressure are variables that should be considered for trying to target sintered densities of 85 % to 90 % T.D. in accordance with the ESA early requirements of the fuel (outlined in § 2.1 of Chapter 1).

The literature has shown that SPS can be used to control the porosity of a sintered compact e.g. by changing the hold times of a sintering profile (Ge et al., 2013). Although this effect could be investigated for the SPS of CeO_2 , this is not a primary objective of the current stage of the ESA programme i.e. it is not one of the ESA early requirements of

the fuel (see § 2.1 of Chapter 1). However, this should be considered at a later stage of the programme.

This review has found that there have been few studies on the sintering of americium oxides and those presented to date have used the cold-press-and-sinter technique.

No definitive conclusions can be made about how lath-shaped CeO_2 or AmO_2 may cold-press-and-sinter based on the PuO_2 study by Bickford et al. (1976).

Finally, the literature review has highlighted that Vickers hardness, flexural strength and Young's modulus are some of the few mechanical properties reported in the literature for nuclear materials. However, Vickers hardness was the most readily reported, according to the literature review. This is likely to be because it can be used to test small samples (see Chapter 4 for more details). Chapter 4 describes Vickers hardness and how it is used to test ceramics.

6. Required Statements for Image Reuse

In accordance with the image reuse permission for Figure 3.9 (Sari et al., 1970), it is required that the source be acknowledged specifically in the following way:

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CHAPTER 4: ANALYSIS TECHNIQUES FOR OXALATE/OXIDE POWDERS & SINTERED BODIES

1. Introduction

Several analytical techniques and one mechanical testing method were used during the course of this study. In Chapter 5, X-ray fluorescence; powder X-ray diffraction; Raman spectroscopy; scanning electron microscopy and laser diffraction particle size analysis were used to analyse the Ce Nd oxalates and/or oxides. Scanning electron microscopy, and Vickers hardness testing were used to analyse sintered surrogate oxides as described in Chapter 6. Finally, Chapter 7 focuses on the Rietveld refinement (see § 2.2) of powder X-ray diffraction data. This chapter provides an introductory insight into each of these analytical techniques and mechanical testing methods. However, only a brief introduction into powder X-ray diffraction data analysis is presented in this chapter. The more detailed background knowledge behind Rietveld refinement is provided in Chapter 7 together with the results of the data analysis.

2. Analytical Methods

2.1. X-ray Fluorescence (XRF) Spectrometry

The explanations provided in § 2.1.1 to § 2.1.3 are based on accounts by Jenkins (1999c) unless specified.

2.1.1. Characteristic X-rays

The powder X-ray diffraction analyses conducted in Chapters 5 and 7 use copper characteristic X-rays as the X-ray source. Chapter 5 also refers to characteristic X-rays when discussing the quantitative XRF analysis of the synthesised Ce Nd oxides.

When a stable atom is subjected to a high energy photon e.g. an X-ray¹⁹, this can provide an inner shell electron with enough energy for it to be ejected from the atom i.e. a photoelectron. The result is a hole in the inner electron shell and the atom being in an unstable (excited) state. To address this instability, one of two effects can occur:

¹⁹ A high energy electron can also cause an inner shell electron to be ejected from an atom.

1. the electrons reconfigure and cause Auger electrons²⁰ to be ejected,
2. or an electron from a higher energy shell moves to fill the hole in the lower energy shell, which results in an X-ray photon being emitted to conserve energy. This is termed fluorescence.

The second effect is explained further: as the energy of each transition level is particular to a given element, so are the energies of its fluorescent X-rays. These X-rays are called characteristic X-rays. X-ray fluorescence spectrometry enables the elemental composition of a sample to be determined. In fact, the photon energy, and hence its wavelength and frequency, is proportional to the difference in energies of the two electron shells involved in the transition (Jenkins, 1999c). Electrons in the higher energy shells have to transition in order to fill the newly created hole from the recently transitioned electron, and fluorescence occurs and so on.

It is common practice to describe an X-ray spectral line using Siegbahn notation, which describes the electronic transition between the two energy levels that caused the X-ray's fluorescence (Tertian and Claisse, 1982). A line that is often referred to when considering X-ray diffraction data is $K\alpha_1$ of copper; many diffractometers use a copper target to create such radiation. The K dictates that an electron from an energy level in a higher shell has been transferred to the K shell and, here, the α signifies that the electron came from L shell. This is sketched in Figure 4.1. However, the transition levels are described not only by the n quantum number but also by l and j . This is the significance of the '1'. The $K\alpha_1$ line in fact describes a transition between the $2p_{3/2}$ and the $1s$ levels.

²⁰ This effect was in fact discovered by Lise Meitner in 1922 but is credited to Auger who independently discovered the effect in 1923.

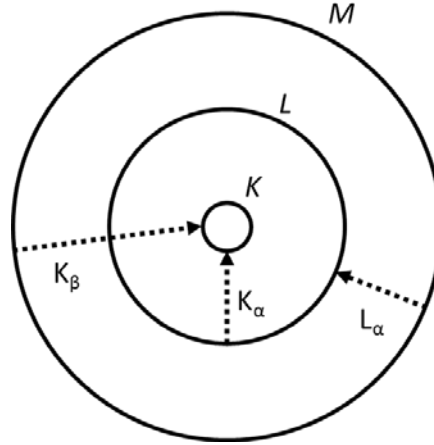


Figure 4.1: A sketch that illustrates the electronic energy transitions between energy shells that result in K_α , K_β and L_α X-ray fluorescence.

An important historical point is that Mosely discovered that there was a relationship between the inverse wavelength of an X-ray and the atomic number of the sample for a given line series e.g. for the $K\alpha_1$ lines, namely,

$$\frac{1}{\lambda} \propto (Z - \sigma)^2, \quad (1)$$

where σ is a screening constant (Tertian and Claisse, 1982).

2.1.2. The XRF Spectrometer

A spectrometer comprises an X-ray tube, which generates the source X-rays. These X-rays impinge on the sample of interest. According to Jenkins and Vries (1969b), a filament is heated by a current, which results in a local electron cloud. A high voltage between its cathode and the anode at the other end of the tube causes the electrons to be accelerated down the tube. On ‘impact’, X-rays are generated, which will escape through the X-ray transparent window. The anode requires cooling as around 99 % of the incoming electrons do not cause X-ray generation. In addition to the characteristic X-rays of the anode material, Bremsstrahlung radiation is produced.

The source X-rays impinge on the sample, which causes it to fluoresce characteristic X-rays. Chapter 5 describes how wavelength dispersive X-ray spectrometry is used for analysing the neodymium and cerium content in synthesised oxide samples (some further details are provided in § 2.1.4). In this type of spectrometry, the emitted characteristic X-rays travel through a collimator. These then strike a single crystal at an angle θ (Scholze

et al., 2006). This is illustrated in Figure 4.2. If the sample contains several different elements, characteristic X-rays of different corresponding wavelengths will be fluoresced (see Mosely's law in § 2.1.1). X-rays of different wavelengths can be detected by varying the angle θ of the crystal, and therefore the angle 2θ of the detector.²¹ For quantitative analysis, the angles θ and 2θ are set to analyse particular spectral lines of interest for the element (Jenkins, 1999a) e.g. Ce $L_{\alpha 1}$.

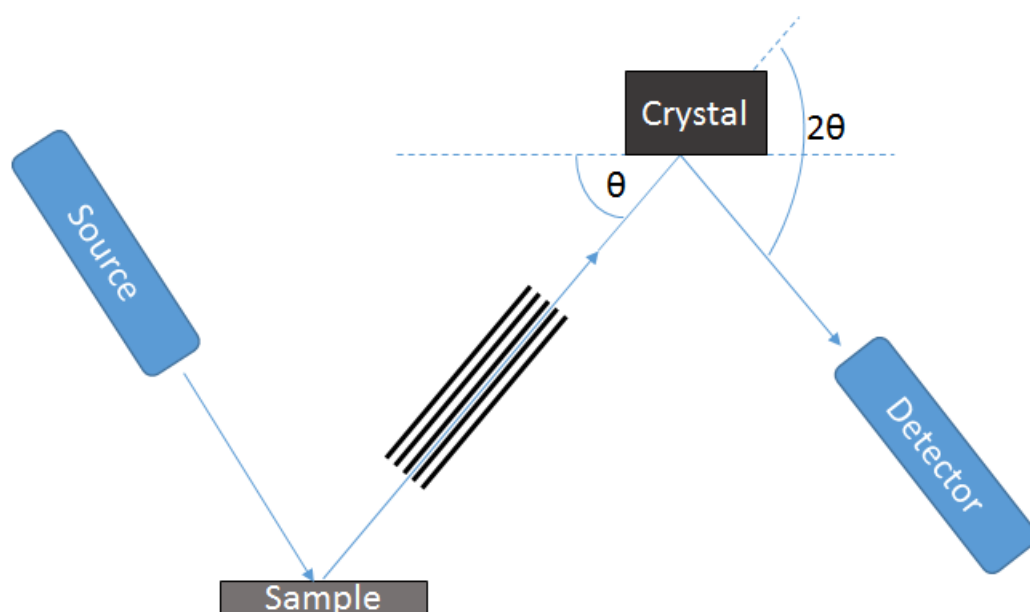


Figure 4.2: A schematic of the geometry of a flat crystal wavelength-dispersive spectrometer.

²¹ The d-spacing of the crystal is well characterised. The diffraction of fluoresced X-rays at a given angle θ will correspond to a wavelength of incident radiation given by Bragg's law of diffraction JANSSENS, K. 2013. Chapter 2.1 X-Ray Based Methods of Analysis. *Modern Methods for Analysing Archaeological and Historical Glass*. John Wiley & Sons Ltd.. Bragg's law is described in § 2.2 of this chapter (Equation 3).

2.1.3. Quantitative Wavelength Dispersive XRF

The term “matrix” is often referred to in quantitative XRF analysis and refers to the mixture of elements present within the sample being analysed (Jenkins and Vries, 1969a). When conducting quantitative XRF analysis, the analyst develops calibration curves with standards of known composition to relate peak intensity to a concentration. Matrix effects are the systematic errors in the results due to the sample. There are four key matrix effects, which are explained briefly in turn based on the description by Jenkins and Vries (1969a) and Jenkins (1999b).

Attenuation of an incident X-ray’s intensity through a sample is sometimes referred to as absorption (Jenkins, 1999c). This convention is adopted in this thesis. The resultant intensity, I , is a function of the mass attenuation coefficient, μ , the sample density, ρ , and the distance, x , that the radiation has travelled through the sample. This function is

$$I(\lambda) = I_0(\lambda)e^{-\mu(\lambda)\rho x}. \quad (2)$$

Attenuation coefficients include the effect of photoelectric absorption of the different energy levels within the different atoms (mass absorption coefficients) as well as the scattering of the incident beam (Jenkins, 1999c). Different elements will have different mass attenuation coefficients. Thus the overall coefficient takes into account the contribution from each element and the relative mass fraction (wt.%) of each (Jenkins, 1999c). The mass absorption coefficient of a given element is a function of the wavelength of the incident radiation. There are discontinuities in the coefficient at particular wavelengths that are known as absorption edges. These relate to photon energies equivalent to the binding energies of electrons in different transition levels (Jenkins, 1999c).

All elements within a matrix will absorb the incident (primary) radiation (Jenkins, 1999b). However, different elements have different absorption curves, which will effectively alter the amount and distribution of primary radiation available to the other elements (Jenkins, 1999b). This can be understood by considering a sample that comprises two elements: A and B, as shown in Figure 4.3. The top of this figure illustrates: the spectrum for the incident radiation of an XRF spectrometer (shaded), the absorption curves for the two elements (labelled by A and B, respectively) and the positions of their characteristic radiation, which have wavelengths λ_A and λ_B , respectively (Jenkins, 1999b). The shaded

area of the middle part of the figure illustrates the primary radiation that element A receives as a consequence of B absorbing a certain fraction of the primary radiation (Jenkins, 1999b). Finally, the bottom part of the figure shows the impact of the absorption by element on A on the primary radiation (depicted by the shaded region) that element B experiences (Jenkins, 1999b). The absorption edge of A causes a discontinuity. The absorption described so far is primary absorption. Absorption of the characteristic radiation of each element also occurs and is called secondary absorption (Jenkins, 1999b). Jenkins (1999b) describes how element A and element B absorb similar amounts of the characteristic X-ray with wavelength λ_B (compare the where λ_B intersects the two absorption curves) and yet how element B absorbs a much higher proportion of λ_A than element A. Thus, this will impact the intensities received by the XRF detector. This is one of the matrix effects for which XRF spectrometers apply corrections.

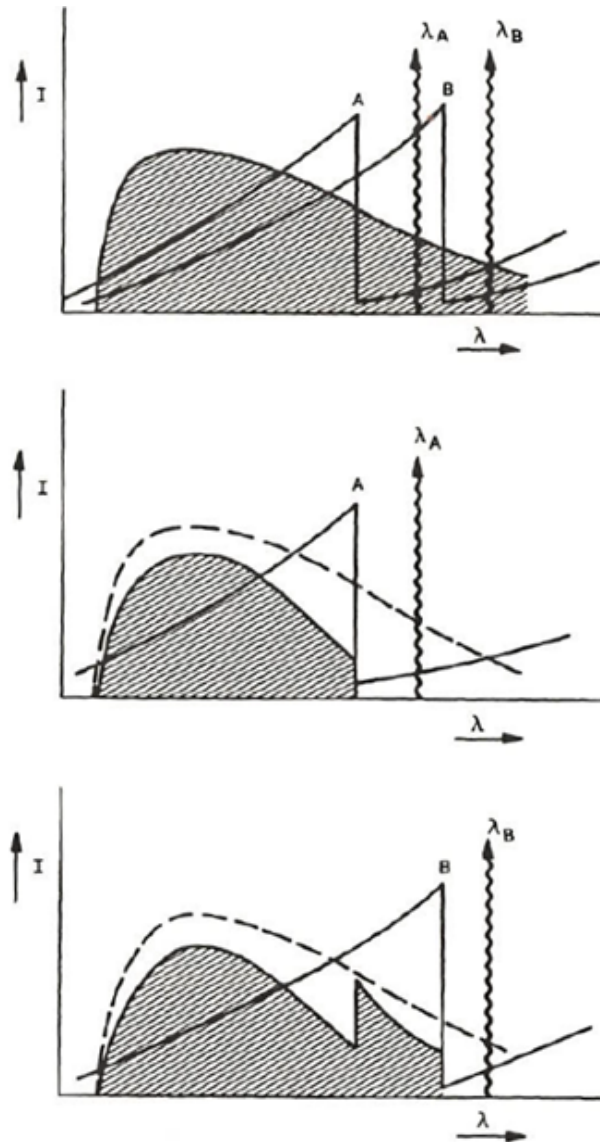


Figure 4.3: Impact of elements A and B in the matrix on the fraction of the overall primary spectrum free for excitation (Jenkins, 1999b)²². Top) shows the primary spectrum of the incident radiation (shaded), elements A's and B's absorption curves and their characteristic radiation positions. Middle) the primary radiation (shaded) that A receives is reduced as B absorbs a certain fraction of the primary radiation. Bottom) the primary radiation (shaded) that B receives is reduced as A absorbs a certain fraction of the primary radiation. The absorption edge of A causes a discontinuity.

²² Permission was granted for reuse from Jenkins et al. (1999). Please see the reference for acknowledgement of the author, book and publisher. The permission requires the copyright notice statement in the book to be duplicated. This is stated at the end of this chapter.

When a non-analyte element (an element not being analysed) in a sample matrix emits characteristic radiation that then causes the element of interest to fluoresce, this is the matrix effect is known as enhancement (Jenkins, 1999b). It essentially causes the analyte element to fluoresce more than would occur if it was only excited by the primary source radiation.

The primary source X-rays (and the characteristic rays from the surrounding matrix) have a limited distance through which they travel in the sample. Thus the corresponding volume of interaction needs to have a composition that is representative of the sample as a whole. If the sample comprises different sized particles with different elemental compositions, some elements could be 'sampled' more than others resulting in more characteristic information being obtained from some elements than from others.

When conducting quantitative XRF analysis, it is essential that the calibration samples and the samples of interest are similar in matrix effects e.g. in mineralogical effects (Stutzman and Heckert, 2013) and in particle size. Yamada (2014) use an example of Al_2O_3 and SiO_2 to describe the concept of the 'mineralogical effect'. The reader is referred to Figure 4.4, which illustrates two mineralogically different samples containing particles of the same size where in a) there is a mixture of the particles of the two separate oxides and in b) the particles are compounds of the two oxides (Yamada, 2014). The mineralogical effect is described in the following sentences, which is based on a description by Yamada (2014). Although each sample contains the same concentration of each species, the detected intensities of the X-rays will differ between samples with different mineralogy. This is because there will be differences in the absorption of characteristic X-rays between the two samples.

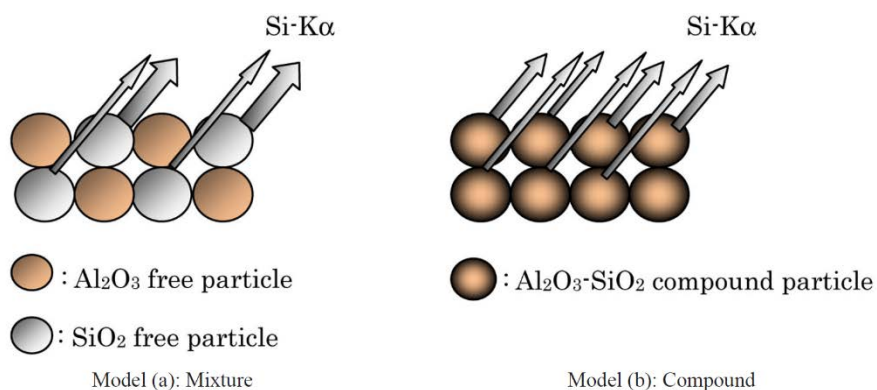


Figure 4.4: An illustration used to describe the impact of mineralogy on X-ray intensities (arrow width) (Yamada, 2014).²³

Differences in particle size within a given sample will mean that there will be a variation in packing within the sample (assuming pressed powder samples are analysed by XRF spectrometry) and that some particles, or grains, will not be exposed to the primary beam and some will be shadowed by larger particles (Yamada, 2014) as shown in Figure 4.5. It is assumed that these factors could cause differences in the fluoresced and absorbed intensities between regions within a given sample, owing to random particle packing. This effect is a greater ‘problem’ for samples of low Z, as the characteristic X-rays will only travel small distances (typically near the sample surface) unlike those generated from higher Z materials (Yamada, 2014).

In this research, the preferred method was to prepare the calibration samples (comprising a mixture of CeO_2 and Nd_2O_3 ; see § 2.1.4) and the synthesised samples of interest (expected to be $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ solid solutions) using the fusion bead method. This would enable them to be prepared with similar matrix effects. The fusion bead method requires relatively small amount of sample to be used (compared to pressed powder pellets described above) e.g. fractions of a gram. The method aids sample homogeneity in the case of samples with heterogeneous composition, it mitigates mineralogical effects and also particle size differences (Jenkins and Vries, 1969c). The method is also useful if the sample size is relatively small and not sufficiently large to create pressed pellets whose

²³ Reuse permission from Rigaku was provided.

diameters are appropriate for the spectrometer. This was the case for the calibration and synthesised samples for this research.

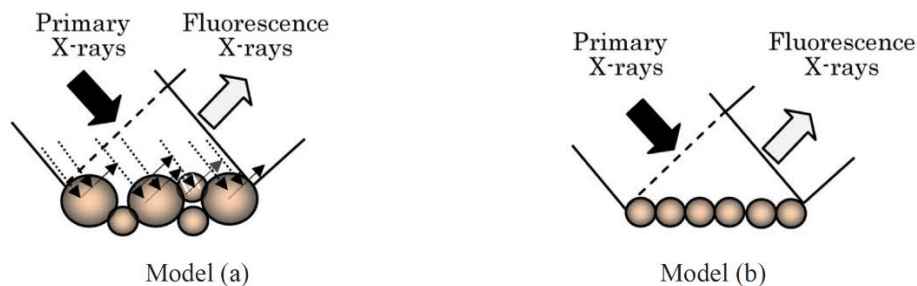


Figure 4.5: Illustrates the effect of different particle sizes on the resultant X-ray fluorescence intensities. Larger particles can shadow smaller particles, which could result in reduced fluorescence and different absorption (Model (a)) to a sample that comprises particles of uniform size (Model (b)).²³

The fusion bead process involves heating a powder mixture of the sample of interest with a 'flux', such as lithium tetraborate, to a high temperature in a crucible. Jenkins and Vries (1969c) concisely state that the fusion process acts to create a solution of all compounds in the mixture by their chemical reaction to create a melt which is then cooled to form a glass-bead, which is void of crystallinity i.e. amorphous so that the mixture is homogeneous.

2.1.4. Calibration curves developed for analysing $Ce_{1-x}Nd_xO_{2-(x/2)}$

Calibration curves were produced in order to quantify the Ce and Nd ion concentrations in each of the calcined oxalate batches, which were expected to be $Ce_{1-x}Nd_xO_{2-(x/2)}$ solid solutions (see Chapter 5). High purity cerium oxide and neodymium oxide were heated in air at 950 °C in a box furnace to dehydrate the materials, to remove any volatiles and to ensure the materials were in their CeO_2 and Nd_2O_3 stoichiometric phases. Each rare earth oxide (REO) is known to be slightly hygroscopic according to publicly available material safety data sheets. Different predefined masses of high purity CeO_2 and Nd_2O_3 were measured to make calibration fusion beads with different wt.% of CeO_2 and Nd_2O_3 . The total sample mass was 0.1 g. Lithium tetraborate was used as the flux, of which 3.0000g was used. These beads were then analysed where the intensities of the isolated Ce $L_{\alpha 1}$ (4.8402 KeV) and the Nd $L_{\beta 1}$ (5.7216 KeV) lines were measured and corrected for matrix and background effects. The matrix was stated to be CeO_2 and Nd_2O_3 as the Ce and Nd ions in the fusion melt would have fully oxidised. This was expected to also

be the case for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ solid solution samples of interest. A PANalytical Axios Advanced X-Ray Fluorescence wavelength-dispersive spectrometer equipped with a 4 kW Rh anode window tube was used to analyse the samples. It is designed to analyse fused beads 32 mm in diameter. The data were analysed using the software provided with the instrument (PANalytical SuperQ system with IQ+). The method used required 0.1 g of sample and 3.0000 g of lithium tetraborate flux (loss on ignition was accounted for) per fused bead. Calibration curves of corrected detected rare earth (RE) counts against the mass percentage of the RE in the sample (denoted by C(Chem)) were produced as shown in Figure 4.6.

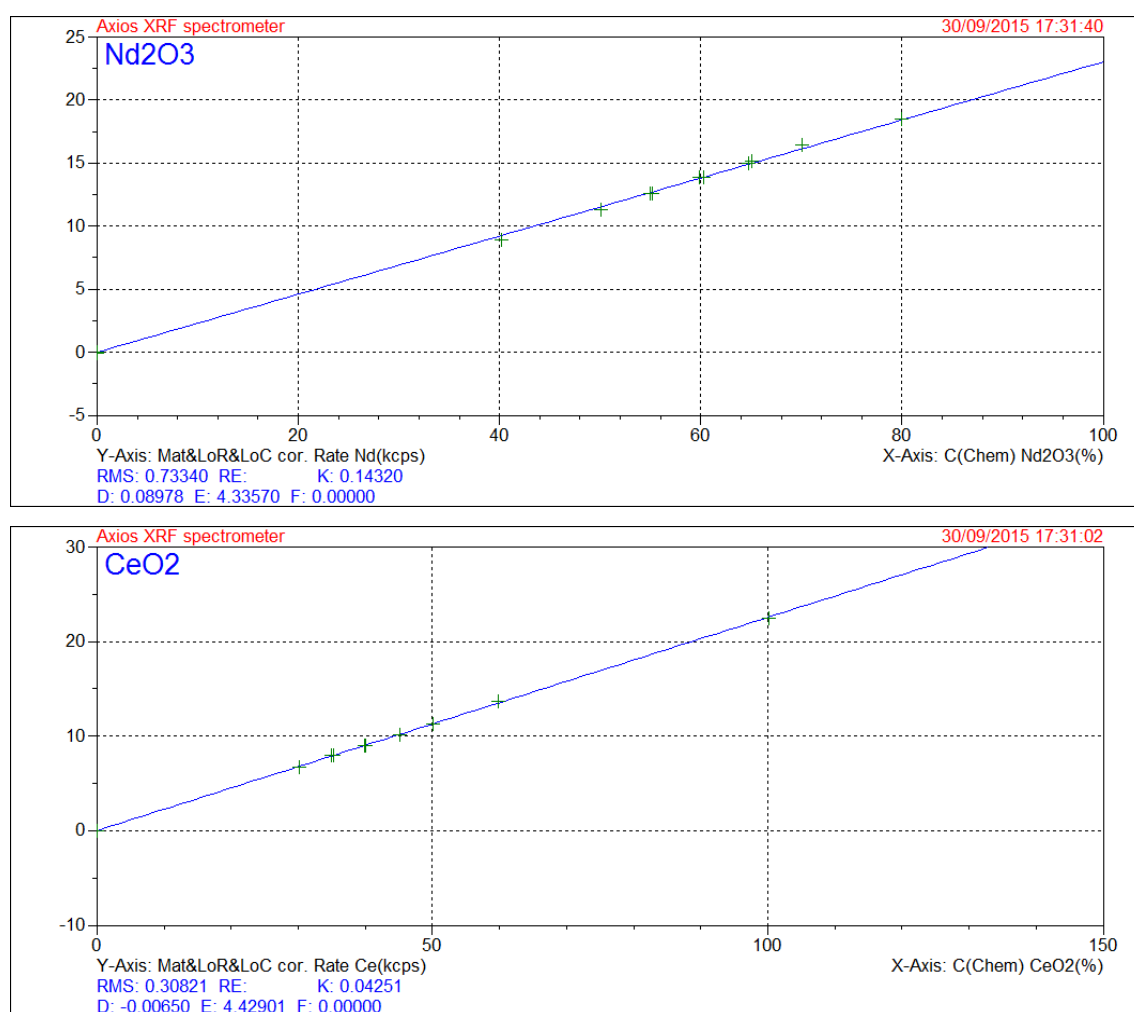


Figure 4.6: calibration curves of XRF counts to corrected RE oxide weight percentage for Nd_2O_3 (top) and CeO_2 (bottom). The root mean square of the fit (RMS), the vertical axis intercept (D) and the gradient (E) of the linear fit are shown for each graph.

The mass percentages of CeO₂ and Nd₂O₃ did not need to be converted into Ce and Nd molar percentages to determine the x-values of the calibration beads but this was important in determining the x-values of the fused beads made from the (expected) Ce_{1-x}Nd_xO_{2-(x/2)} solid solutions. Details of how this was conducted are found in Chapter 5.

2.2. Powder X-ray Diffraction (PXRD)

According to Cullity and Stock (2001) a crystal is a solid with a three dimensional periodic arrangement of ions, atoms or molecules. X-ray diffraction allows the crystal structure to be analysed. The incident X-rays interact with the electron clouds of the periodic array of atoms, and diffract (Pfennig, 2015). “A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing one another” (Cullity and Stock, 2001).

An example of an X-ray diffraction pattern is illustrated in Figure 4.7. The intensity of the scattered X-rays is plotted against an angle 2θ . The peaks of maximum intensity are known as diffraction peaks and correspond to the constructive interference of scattered X-rays (Lou, 2011). Their 2θ positions are described by Bragg’s law, which requires that the path difference between an incident and reflected ray is an integral number of wavelengths. The law is as follows

$$n\lambda = 2d \sin \theta, \quad (3)$$

where n is an integer, λ is the wavelength of the incident radiation, d is the interplanar distance and θ is the diffraction angle as shown in Figure 4.8. Each peak corresponds to diffraction from parallel crystallographic planes designated by the Miller indices hkl . The interplanar distance d , which is often commonly referred to as the ‘ d -spacing’, is related to the Miller indices via the lattice parameter(s), or unit cell parameter(s), according to the crystal system via standard relations (Smart and Moore, 2012). For the case of a cubic system with a unit cell parameter a , the relation is

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}. \quad (4)$$

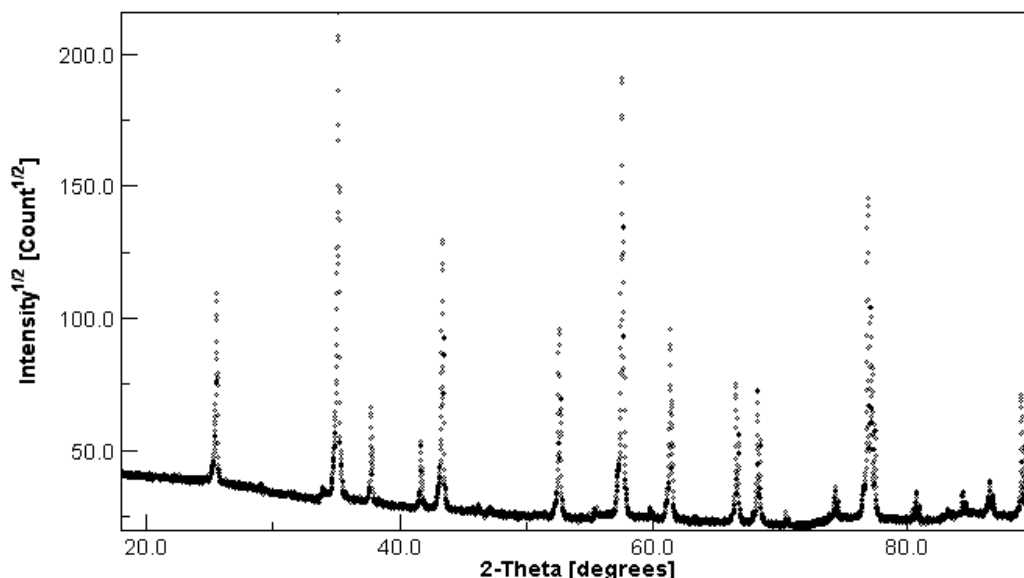


Figure 4.7: An example of a powder X-ray diffraction pattern. This pattern was generated by analysing Al_2O_3 , which had a corundum structure (see Chapter 7).

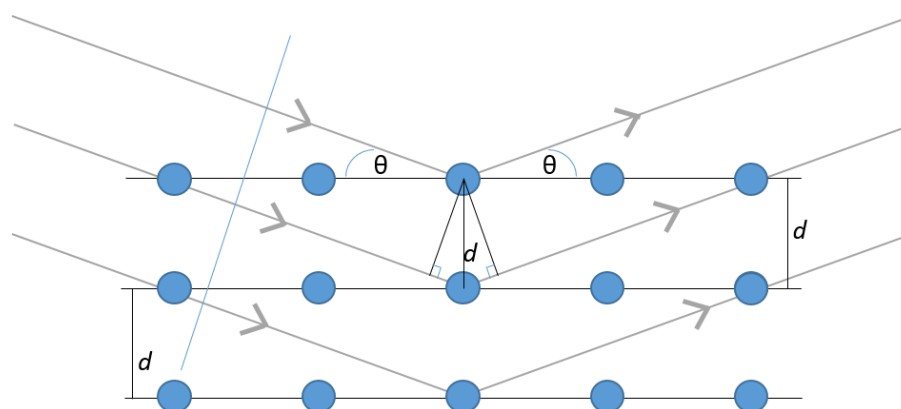


Figure 4.8: the geometry behind Bragg's law. For simplicity, let the circles represent atoms and the horizontal lines represent atomic planes. The rays are X-rays.

The diffraction pattern of a sample is a fingerprint (Mittermeijer, 2011) that is unique to that arrangement of atoms. The recorded pattern is compared to records in large databases that are open access such as those owned by the International Centre for Diffraction Data® (ICDD®). An inference can then be made about the structure and owing to the fingerprint nature of the patterns, what the sample is. As an example, pattern matching was used to analyse the synthesised Ce Nd oxide solid solutions as described in Chapter 5.

A recorded X-ray diffraction pattern not only reflects the crystallographic structure of the sample, but also incorporates other effects, such as the response of the diffraction instrument, whether the crystallographic planes of the sample have a preferred orientation, and the size distribution of the crystallites. Rietveld refinement allows these various contributions to the diffraction pattern to be modelled in order to allow a precise determination of the crystallographic parameters of interest. Chapter 7 provides a more detailed explanation of the theory behind Rietveld refinement and how this analysis technique has been used to analyse a Ce Nd oxide solution.

Finally, as mentioned in § 2.1.1, X-ray diffraction data are often recorded using diffractometers with a copper target. The generated X-rays are $\text{CuK}\alpha_{1,2}$ and $\text{K}\beta$. The $\text{K}\beta$ radiation is typically filtered out using a nickel target and although $\text{CuK}\alpha_{1,2}$ remains, it is the $\text{CuK}\alpha_1$ radiation that is of interest; when the positions of diffraction peaks are compared to those in databases, such as those mentioned above.

2.3. Raman Spectroscopy

Unlike X-ray diffraction analysis, vibrational spectroscopy cannot be used to determine the structure of a material directly (Carabatos-Nédelec and Smith, 2001). However, the structure can be inferred by comparing the fingerprint of the spectrum to that of a material whose structure is known (Carabatos-Nédelec and Smith, 2001).

Raman spectroscopy is a form of vibrational spectroscopy. The instruments typically have a monochromatic laser source, which is used to excite a sample (Larkin, 2011). Figure 4.9 illustrates that there are two types of Raman scattering: anti-Stokes and Stokes, where, respectively, the emitted photon has a higher and lower frequency than that of the incident radiation (Larkin, 2011). Raman scattering is thus an inelastic process unlike Rayleigh scattering (Larkin, 2011). In anti-Stokes Raman scattering, the sample is initially in its first excited vibrational state before it absorbs an incident photon, whereas in Stokes Raman scattering, the sample is initially in its ground vibrational energy state as shown by Figure 4.9 (Larkin, 2011).

Both Rayleigh and Raman scattering occur when a sample is subjected to a laser source. According to Larkin (2011), the former is much more probable with its intensity being around 10^{-3} of that of the incident radiation (c.f. the fractional intensity is 10^{-6} for Raman scattering). The incident radiation induces a dipole moment in a molecule (Larkin, 2011).

For Raman scattering to occur, the polarisability of a molecule must change during vibration (Smith, 2013, Kraft, 2006). It is important to highlight that crystalline solids can also be analysed using Raman spectroscopy.

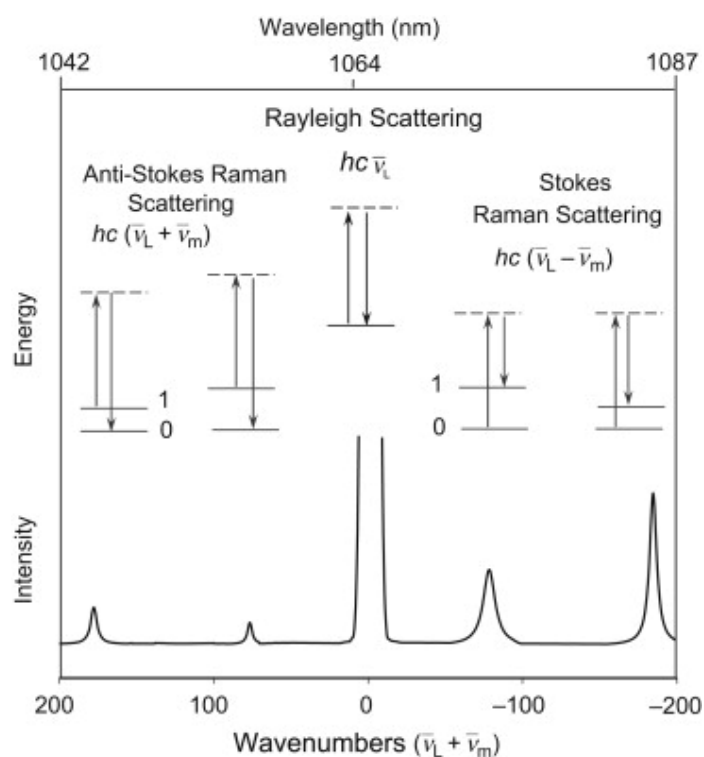


Figure 4.9: Illustrates a schematic of Raman and Rayleigh scattering. Up arrows correspond to the incident laser with frequency ν_L (wavenumber $\bar{\nu}_L$). Virtual states are depicted as dashed lines. In Raman scattering, the resultant photon has an increased (anti-Stokes) or decreased (Stokes) frequency and hence wavenumber as shown.²⁴

Horlait et al. (2011) used Raman spectroscopy to characterise CeO_2 and $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-(x/2)}$ solid solutions (Ln refers to lanthanides) with particular emphasis on $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ using a He-Ne 633 nm laser. Figure 4.10 illustrates the collected spectra for oxides with a range of compositions. A general feature of Raman spectra is that the intensity is plotted against the Raman shift i.e. the shift in wavenumber relative to that of the incident radiation (Vadgama and Peteu, 2013). In Figure 4.10, Horlait et al. (2011) have labelled the bands that are characteristic of CeO_2 , F-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$, C-type oxides and

²⁴ Reprinted from Infrared and Raman Spectroscopy, Larkin P., Chapter 2 - Basic Principles, Page 19, Copyright (2011), with permission from Elsevier.

A-type Nd_2O_3 . In Chapter 5 of this thesis, acquired Raman spectra of synthesised Ce Nd oxalates and their oxides are presented together with their determined band positions. These data are compared to those in the literature, such by Horlait et al. (2011), to infer the oxide constituents. The results are also compared to X-ray diffraction data.

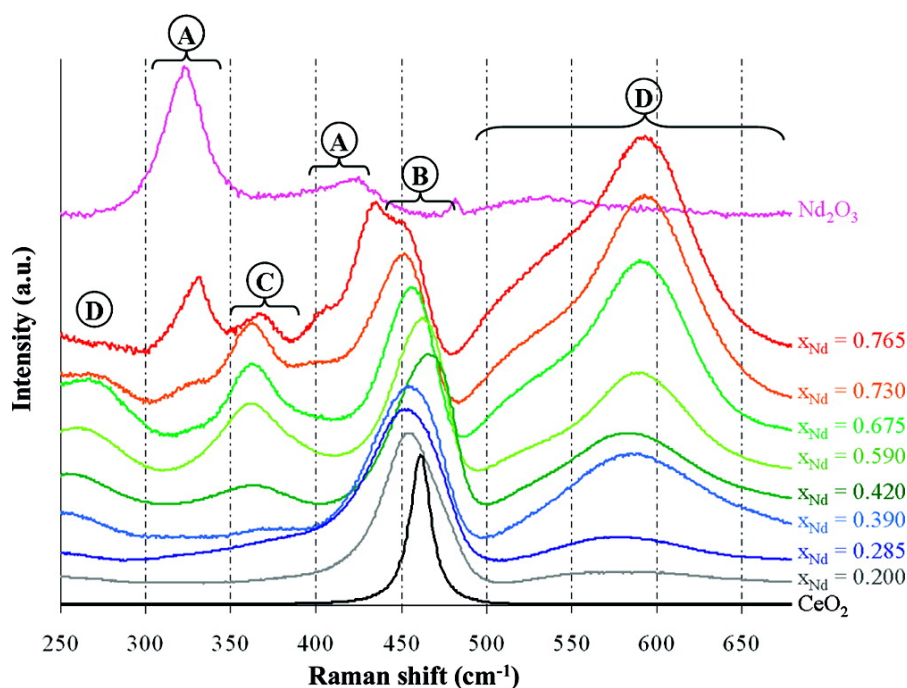


Figure 4.10: illustrates the micro-Raman spectra recorded by Horlait et al. (2011) for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a range of x -values. Each band corresponded to fingerprints of different oxide phases, namely, A) A-type Nd_2O_3 ; B) the F_{2g} vibration mode of CeO_2 and the F-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$; C) a C-type structured oxide and D) oxygen vacancy related structure.²⁵

2.4. Scanning Electron Microscopy (SEM)

Observing the surface topography of a sample at the micrometric (and under) scale can be conducted using a scanning electron microscope. Such instruments are common place in laboratories despite their high cost. In this section, a basic introduction to the technique is provided, which is based on the explanations by Khursheed (2010) and Goldstein et al. (2003).

²⁵ Reprinted with permission from Horlait et al. 2011, *Inorg. Chem.*, **50**, 7150-7161. Copyright (2011) American Chemical Society.

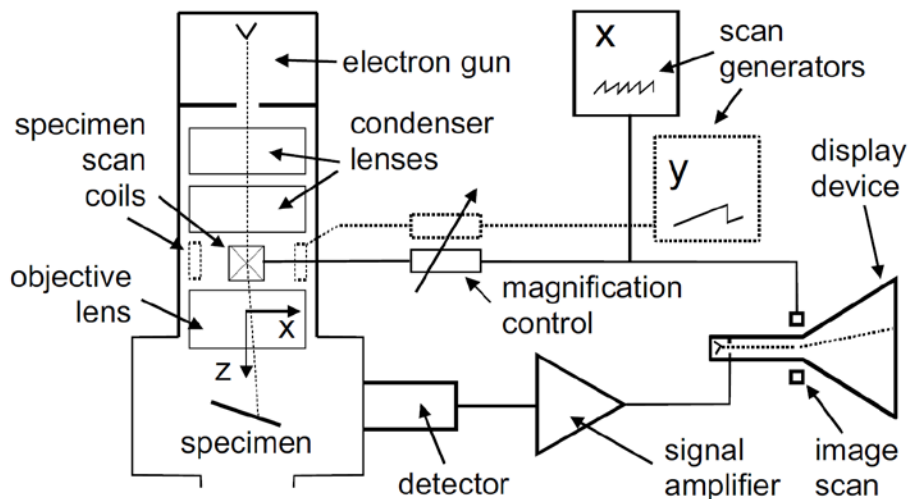


Figure 4.11: Schematic diagram of a scanning electron microscope with a CRT display.²⁶

The components of an SEM instrument are presented in Figure 4.11. The system runs under vacuum. According to Goldstein et al. (2003), the electron beam that is generated by the electron gun would have too large a ‘spot size’ on the sample to create a focussed image. Consequently, electromagnetic lenses are employed between the gun and sample to demagnify the beam to an acceptable diameter of 1 to 10 nm with a current of 1 to 100 pA of interaction with the sample to an around 1 μm depth (Goldstein et al., 2003, Khursheed, 2010). All three lenses depicted in Figure 4.11 act like condenser lenses i.e. act to demagnify the beam, despite the third being called an objective lens. The function of this third lens is to tune the spot size (Bozzola and Russell, 1999). Accelerating voltages ranging from 0.1 to 30 kV are used (Goldstein et al., 2003). The beam is rastered across the specimen by electromagnetic scan coils in the objective lens and the scan signal

²⁶ Springer Physical Principles of Electron Microscopy, The Scanning Electron Microscope, 2005, p. 126, R. F. Egerton, (© 2005 Springer Science+Business Media [Please see the end of this chapter for the full copyright notice, which the terms and conditions of this reuse license requires.]) With permission of Springer.

CRT stands for cathode ray tube and the image reuse terms and conditions require the image caption to be restated exactly according to that of the original image source.

is outputted to a computer monitor in synchronous (Goldstein et al., 2003, Khursheed, 2010) for the operator to see.

X-rays (characteristic and Bremsstrahlung) and electrons are emitted from a sample as a result of its interaction with the electron beam. Secondary electrons (SE) have energies less than 50 eV and backscattered electrons (BSE) have even higher energies e.g. up to that of the primary beam (Khursheed, 2010). The former are the result of inelastic interactions as opposed to elastic interactions that result in BSE. The SEM can be used in the SE or BSE. The relative atomic number of the specimen e.g. high or low, can be inferred by detecting either of these types of electrons. According to Bozzola and Russell (1999), higher Z elements appear brighter than lower Z elements. The contrast is small when secondary electrons are detected but much greater for backscattered electrons Bozzola and Russell (1999).

Finally, a practical aspect is mentioned briefly. When a specimen that is an electrical insulator undergoes SEM it often exhibits ‘charging’. This is the result of electron accumulation. This can result in spurious effects, such as apparent bright patches, stretching of a sample in one or more directions or the apparent movement of the sample across the display screen. This effect is mitigated by improving the conduction path of the electrons e.g. by gold-coating the sample and applying silver-dag (Echlin, 2009).

2.5. Laser Diffraction Particle Size Analysis

The following explanation is based upon Chapter 6 of NIST Particle Size Characterisation Recommended Practice Guide (NIST et al., 2001): laser diffraction is a non-imaging technique that relies on the light scattering of particles to determine their diameters. The dedicated instruments often use algorithms that assume: the particles are spherical; multiple scattering does not occur (see Glossary for further details) and the detected scattered pattern is the sum of the individual scattering patterns from each particle resulting from the interaction with the incident beam. The detected scattering pattern is deconvolved into the individual patterns from each particle. Each of these patterns is inverted to calculate the particle size (diameter). The algorithm that is used to conduct this deconvolution is specified by the ‘optical model’. In commercial instruments, the user can choose an optical model based on Mie theory or on its Fraunhofer diffraction approximation. The algorithms used to conduct these calculations by the software specific to commercial instruments will often have some propriety variation from the theory. A

brief introduction to Mie theory is provided before the condition for using the Fraunhofer diffraction approximation is described. The choice of optical model depends on the sample of interest.

Bohren and Huffman (1983) provided a mathematical account of Mie theory (that spans tens of pages) in which Maxwell's equations were solved to derive the intensity of light scattered from a spherical particle of known refractive index in a medium with known refractive index. In addition to the particle morphology, the theory assumed the particles were homogeneous and isotropic (Wriedt, 2012), and that their refractive index as well as that of the containing medium were known (Horiba Scientific, 2016, Beckman Coulter, 2011). The refractive index of the sample is given by a complex number, namely,

$$m = n_r - in_i, \quad (5)$$

where real n_r is the real refractive index component and n_i is the imaginary component. The imaginary component describes the light absorption, and is also affected by surface roughness and heterogeneity in the density of the sample (NIST et al., 2001). It is often difficult to obtain accurate values for the imaginary refractive index of a material. Choosing an optical model based on Mie theory requires that the complex refractive index of the material as well as that of the surroundings must be specified. Such information is not required if the Fraunhofer approximation is used.

The derived intensity of the scattered unpolarised light (NIST et al., 2001) is given by

$$I(\theta) = \frac{I_0}{2k^2a^2} [[S_1(\theta)]^2 + [S_2(\theta)]^2], \quad (6)$$

where I_0 is the incident light intensity, k is the wavenumber, a is the distance of the particle from the detector and, finally, S_1 and S_2 are functions which, according to NIST et al. (2001) describe the “change in amplitude of the perpendicular and parallel polarized light as a function of the angle θ , measured in the forward direction.”

Unlike with Mie theory, the Fraunhofer approximation does not require the refractive index of the sample nor that of its surroundings to be specified. The analyst must choose an optical model that is appropriate for the sample of interest. Essentially, this is a question of whether the particle size is sufficiently large that the condition of the

Fraunhofer diffraction approximation can be applied; the Fraunhofer diffraction approximation requires the diameter of the spherical particle to be much greater than the wavelength of the incident radiation (NIST et al., 2001). The literature states various values for the lower particle diameter limit for which the Fraunhofer approximation is applicable. Although NIST et al. (2001) and NPL et al. (2009) state that the Fraunhofer approximation can be used for particles with diameters greater than 1-2 μm , other sources such as the ISO 13320 1999 standard for particle size analysis by laser diffraction suggests that the lower limit is 50 μm and that Mie theory should be used for smaller particles (Jones, 2003). Horiba Scientific (2016), who is an instrument manufacturer, states that the accuracy of the Fraunhofer approximation for estimating spherical particle diameter is compromised below 20 μm . To be conservative, it is assumed that the Fraunhofer approximation should not be used for samples with particles sizes as low as 20 μm and thus Mie theory should be used.

As was previously stated, Mie theory describes the scattering of light by spherical particles and calculations use the volume of the sphere. The calculated particle size is that of a sphere with an equivalent volume (NPL et al., 2009, NIST et al., 2001). Laser diffraction instruments thus infer the equivalent diameters of a spheres that would scatter to provide the detected light intensity (Horiba Scientific, 2016). Typically, particle size distributions are reported as differential volume (%) distributions, which describe the “relative percentage frequency distribution (by volume) and thus can be used to estimate the relative amounts of particles of different size ranges” (NIST et al., 2001).

Other data that are often reported in addition to the differential particle size distribution are the d_{10} , d_{50} and d_{90} values, which represent the particle sizes below which 10 %, 50 % and 90 % of the distribution exists, respectively (NPL et al., 2009, NIST et al., 2001). The d_{50} value therefore corresponds to the median particle size. Their locations in a symmetric particle size distribution are shown in Figure 4.12a. When the particle size distribution is asymmetric, the position of the peak no longer corresponds to the median particle size but instead to the modal particle size as shown in Figure 4.12b.

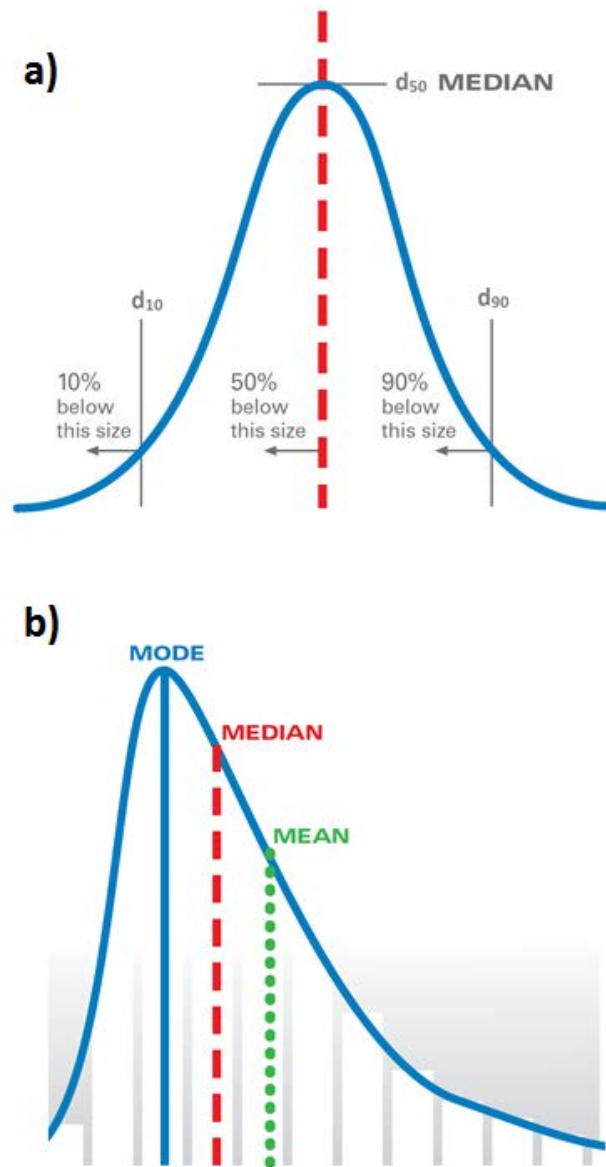


Figure 4.12: schematics illustrating a) the locations of d_{10} , d_{50} and d_{90} values in a symmetric particle size distribution (adapted from Figure 5 in the guidebook by Horiba Scientific (2016)), and b) the positions of the mode, median and mean particle sizes in an asymmetric particle size distribution.²⁷

²⁷ Permissions were obtained from Horiba for the reuse of these figures. Figure 4.12a) is adapted from Figure 5 in the “A Guidebook to Particle Size Analysis” HORIBA SCIENTIFIC 2016. A Guidebook to Particle Size Analysis.

According to Beckman Coulter (2009), “[l]arge particles scatter light strongly at low angles and with readily detectable maxima and minima in the scattering pattern” and “small particles scatter light weakly and without any discernible maxima and minima until extremely high angles of measurement are reached”. An analyser will contain several detectors at specific locations that cover a large angular range (NIST et al., 2001, Horiba Scientific, 2016).

Polarization Intensity Differential Scattering (PIDS) analysis allows the size of submicron particles to be determined (Beckman Coulter, 2011). A more detailed description of the technique can be found in the referenced texts by Beckman Coulter (2011) and Xu (2002) but a basic introduction is provided here based on a description by these authors and Meritics Ltd. (2015):

The PIDS method essentially relies on the fact that an oscillating dipole moment is induced in particles whose sizes are much smaller than the wavelength of the incident light causing the induction. It results from the interaction with the light’s electric field. The electrons move in the plane of the oscillating electric field and therefore perpendicular to the light’s propagation direction. The result is that “the oscillating dipole radiates light in all directions except in the direction of oscillation” (Xu, 2002). Thus in order to detect the light, the detector must not be aligned in this oscillation direction (Xu, 2002). According to Meritics Ltd. (2015) the technique involves shining vertically and horizontally polarised light separately on the sample and measuring the intensities of the scattered light in these two polarisations at different angles. The intensity difference is then calculated at these different angles and the result is known as the PIDS signal. The signal, however, is wavelength dependent. Light sources of multiple wavelengths are used by Beckman Coulter laser diffractometers (the manufacturer of the instrument used in this study of Ce Nd oxalates). The resulting PIDS signal versus scattering angle data is converted into intensity versus scattering angle data, which the instrument then interprets using the algorithm it uses for non-PIDS data to determine the resulting particle size distribution (Meritics Ltd., 2015).

The LS Coulter 230 laser diffraction system (Beckmann Coulter), which was used for the investigation, uses a laser light source with a 750 nm wavelength (but three wavelengths for PIDS). As will be shown in Chapter 5, scanning electron microscopy of the synthesised Ce Nd oxalate particles indicated that they had lath morphologies with

lengths typically several tens of micrometres (their widths and thicknesses were shorter; see Chapter 5). It was thus concluded that an optical model based on Mie theory and not on the Fraunhofer approximation needed to be used. Additionally, the non-spherical nature of the particles mean that the exact values of the particle sizes e.g. d_{50} will be less accurate than if they were spherical (NPL et al., 2009). In practice, the majority of samples analysed using such instruments are not spherical. Bohren and Huffman (1983) states Mie theory can provide a first-order approximation of the “optical effects in nonspherical particles”.

3. Mechanical Testing Methods

3.1. Vickers Hardness

Hardness is a property that describes the resistance of a material to indentation. The property is often simple to measure making it a popular property to quantify for materials. Hardness tests can be performed on small samples of materials and on larger components. They are non-destructive tests that can be used for quality assurance on production parts. For ductile materials such as metals, some methods of measuring hardness generate values that can be correlated approximately with yield strength. Consequently, hardness testing machines are commonly found in mechanical testing facilities across the world.

Hardness testers apply a fixed force to the material through an indenter of defined shape. The area or depth of the resulting indentation is measured, with a harder material indicated by a smaller indentation from a given force. Several standard force ranges may be used for hardness testing. It is fairly common practice for operators to describe a load using kilogram-force or gram-force units (kgf or gf) or solely by referring to the mass that provides the load. Typically, macrohardness refers to test that have used loads greater than approximately 1 kgf. Such tests give an indication of the bulk properties of a material. Loads from around 1 gf to 1 kgf are typically termed microhardness and can be useful to measure the variation in hardness across microstructural features, for example within the grain and at the grain boundary region.

The measured hardness of a ceramic is a function of the load used to make the indentation. A document by the National Physical Laboratory (Morrell, 1990) states that this effect is noticeable in Vickers and Knoop tests that use loads less than 1 kgf. This is known as the indentation size effect (Quinn et al., 2004). Consequently, only data measured using the

same conditions, which includes the load, should be compared. The other difficulty that arises from using low loads is the smaller resulting indents, which will have greater relative uncertainties in indentation dimensions (Danzon et al., 2013). Loads of 1 kgf are often preferred for Vickers hardness to help mitigate the indentation size effect; to have lower relative uncertainties in dimension measurements and to try to avoid cracking (Danzon et al., 2013, Morrell, 1990).

There are many different methods for testing hardness such as Brinell, Vickers, Knoop and Rockwell. The Brinell and Rockwell indenters are spherical and the Vickers and Knoop indenters are pyramids. A schematic of the geometries of the pyramid indents are shown in Figure 4.13. In the Rockwell method, the depth of the indenter's penetration into a specimen under a specified load is measured (Marinescu et al., 1999). For Brinell, Vickers and Knoop an area associated with the indent is measured (Marinescu et al., 1999). Brinell and Vickers hardness test calculations typically use the surface area of an indentation whereas Knoop hardness tests typically use the projected area (Kaufmann, 1999, Marinescu et al., 1999). Despite all methods measuring hardness, the values measured by different techniques cannot be compared as material response is affected by indenter geometry and there is, in general, no way of converting a value measured by one method into an equivalent value measured by a different method to allow comparison (Riedel et al., 2008). In fact, for some test methods, it is advised that only materials tested using the same conditions e.g. load and dwell time, be compared (ASTM C1327 - 08, 2008).

Cracking from the indentation region is a challenge when conducting hardness tests in brittle materials such as ceramics. The ASTM Vickers hardness standard test method for testing advanced ceramics states that as well as potentially making indentation tip identification more difficult, cracking impacts the ways that a material deforms to create the indent (ASTM C1327 - 08, 2008). Brinell and Rockwell hardness measurements are avoided when testing ceramics as their spherical indenters are associated with causing cracking (Callister and Rethwisch, 2012). However, Vickers and Knoop hardness tests, which use pyramid shaped indenters, are typically employed to test ceramics (Marinescu et al., 1999, Callister and Rethwisch, 2012). Measures to reduce cracking during Vickers hardness tests of ceramics include using lower loads or to instead use a Knoop hardness

test as Knoop indentations can cause less cracking measurements owing to its indenter geometry (ASTM C1327 - 08, 2008, Bengisu, 2001).

The Vickers hardness of a Vickers indent is typically quoted in GPa and described by

$$HV = 1.8544 \times 10^{-3} \left(\frac{P}{d^2} \right), \quad (7)$$

where P is the load in Newtons and d is the average of the diagonal lengths (d_1 and d_2 in Figure 4.13) of the indentations (ASTM C1327 - 08, 2008).

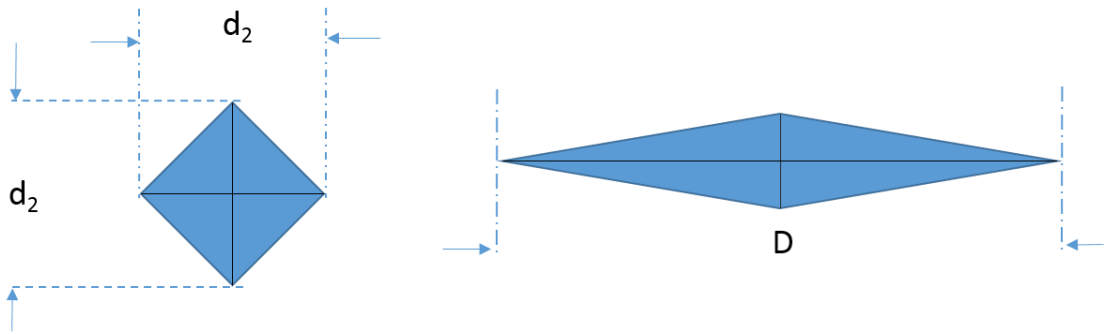


Figure 4.13: Illustrates a Vickers indent (left) and a Knoop indent (right). The dimensions that are measured for each indent when conducting the hardness tests are shown are indicated. The former image is based on the schematic in ASTM C1327 - 08 (2008).

The literature review in Chapter 3 highlighted that Vickers hardness data exist for spark plasma sintered nuclear and surrogate oxide materials, and that this hardness measurement is readily reported unlike Knoop hardness. The approach followed in this study was therefore to test the Vickers hardness of sintered ceramic surrogate oxides as opposed to Knoop hardness to allow comparisons with the literature, between SPS samples and cold-pressed-and-sintered samples. The ASTM C1327 - 08 (2008) standard was used.

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CHAPTER 5: CERIUM NEODYMIUM OXIDE SOLID SOLUTION SYNTHESIS AS A POTENTIAL ANALOGUE FOR SUBSTOICHIOMETRIC AmO_2 FOR RADIOISOTOPE POWER SYSTEMS

This chapter is based upon a paper (Watkinson et al., 2017a) published in the Journal of Nuclear Materials. Please see the Publications page.

1. Introduction

1.1. Surrogates for Americium Oxides

Neodymium (III) oxide (Nd_2O_3) and cerium (IV) oxide (CeO_2) are reasonable surrogates for Am_2O_3 and AmO_2 , respectively, depending on the property being assessed. For example, Table 5.1 shows that Nd_2O_3 and CeO_2 can be considered as suitable crystallographic surrogates. Williams et al. (2013) identified the suitability of Nd_2O_3 as a surrogate for Am_2O_3 by comparing the effective ionic radii (0.975 Å and 0.983 Å, respectively (Shannon, 1976)), the phase transition temperatures, the melting temperatures and the coordination numbers associated with each of their crystallographic phases e.g. cubic and hexagonal. CeO_2 and AmO_2 have similar cationic radii at 0.97 Å and 0.95 Å, respectively (Claparède et al., 2011). Zinkevich et al. (2006) reported a number of values for the melting point of CeO_2 according to various literature reviews and research papers e.g. they mentioned the lowest noted value was measured by Mordovin et al. (1967) to be 2670 K. Zinkevich et al. (2006) preferred to use 3000 ± 20 K (Brewer, 1953) in their Ce-O thermodynamic modelling study as it stated an uncertainty. Thus there is some debate regarding its melting temperature. AmO_2 is likely to have a melting point at around 2448 K (Schulz, 1976). This discrepancy is acceptable as the surrogate materials will not be sintered at temperatures as high as these.

Volume changes associated with crystallographic phase transitions may want to be avoided during sintering. In the context of the ESA programme, it is essential that intact americium oxide discs or pellets can be created with reproducible geometry. Thus such volume changes could make it difficult to densify discs or pellets and potentially cause cracking during the fabrication process. Such effects should also be avoided during integration in radioisotope power systems or in accident scenarios such as launch pad

fires or earth re-entry (to name a few), where structural integrity of the pellet or pellets is an important consideration for the safety case.

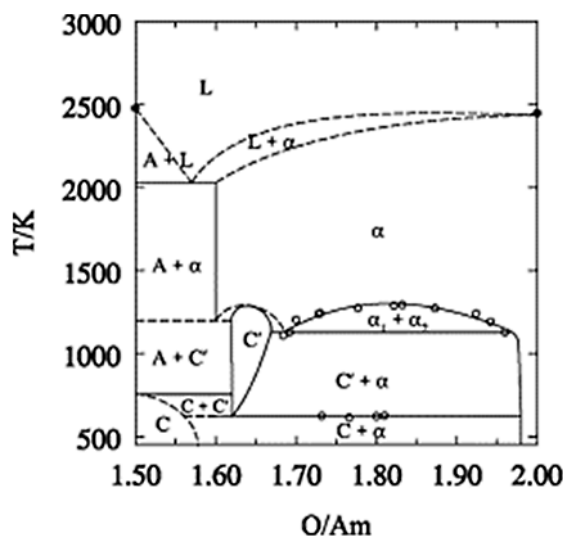


Figure 5.1: The tentative Am-O phase diagram²⁸ by Thiriet and Konings (2003), which also illustrates data (circles) measured by Sari et al. (1970). The C phase corresponds to cubic (Ia-3) Am_2O_3 ; the A phase to hexagonal Am_2O_3 ; the C' phase to a higher temperature cubic (Ia-3) phase and all α phases to face centred cubic $\text{AmO}_{2-(x/2)}$.

The phase diagram (see Figure 5.1) developed by Thiriet and Konings (2003) shows that AmO_2 and a number of substoichiometric americium oxides, $\text{AmO}_{2-(x/2)}$, are cubic (unlike Am_2O_3) across a range of temperatures that could be suitable for sintering trials. Thus crystal system changes could be avoided by using these oxides. One option would be to sinter an $\text{AmO}_{2-(x/2)}$ phase that remains cubic with a variation in temperature. A single cubic phase crystal with an O/Am ratio between 1.65 and 1.75 has been chosen as a preferred starting point. Intermediary oxidation states of americium oxide with particular oxygen-to-americium ratios would be targeted by controlling the oxygen potential and the temperature of the sintering environment. This would require the use of different gaseous environments, such as hydrogen, to provide reducing environments. Sari and Zamorani (1970) have provided some insight into how this could be achieved.

²⁸ Reprinted from Journal of Nuclear Materials, Vol 320, Chemical Thermodynamic Representation of AmO_{2-x} , Pages 292-298, Copyright (2003), with permission from Elsevier.

Table 5.1: the different crystal structures of Am(IV) and Am(III) oxides, and some of their associated surrogates. Note there are discrepancies about the structures of A-type phases. FCC and BCC refer to face centred cubic and body centred cubic, respectively.

Am oxide	Symmetry	Space Group	Lattice Param. Lengths (Å)	Surrogate	Symmetry	Space Group	Lattice Param. Lengths (Å)
AmO ₂	FCC (fluorite-type) (Thiriet and Konings, 2003)	Fm-3m (Okamoto, 2011) *	5.374 (Runde and Wallace, 2008)	CeO ₂ (Horlait et al., 2011)	FCC (fluorite-type) (Horlait et al., 2011)	Fm-3m (Horlait et al., 2011)	5.41134(8) (Horlait et al., 2011)
A-Am ₂ O ₃	Hexagonal (Morss, 1991)	P-3m1 (Morss, 1991)	a ₀ =3.817 c ₀ =5.971 (Morss, 1991)	A-Nd ₂ O ₃	Hexagonal (Horlait et al., 2011)	P-3m1 (Horlait et al., 2011) +	a ₀ =3.83120 c ₀ =6.00170 PDF 01-079-9858
	Hexagonal (Lebreton et al., 2012)	P6 ₃ /mmc c (Lebreton et al., 2012)			Hexagonal (Navrotsky and Ushakov, 2005)	P6 ₃ /mmc (Navrotsky and Ushakov, 2005)	
B-Am ₂ O ₃	Monoclinic (Runde and Wallace, 2008)	C2/m (Runde and Wallace, 2008) ^Δ	a ₀ =14.38 b ₀ =3.52 c ₀ =8.92 (Runde and Wallace, 2008)				
C-Am ₂ O ₃	BCC (Runde and Wallace, 2008)	Ia-3 (Lebreton et al., 2012)†	11.03 (Runde and Wallace, 2008)	C-Nd ₂ O ₃	BCC (Frohlich et al., 2006)	Ia-3 (Frohlich et al., 2006, Artini et al., 2014)	11.1 (Frohlich et al., 2006)

* † Unit cell illustrations can be found in Figure 8.9 (p. 1358) by Runde and Wallace (2008).

+ Δ Unit cell illustrations of the (rare earth) surrogate oxides can be found in Figure 3.16 (p. 74) by Schweda and Kang (2005). It is noted that Chikalla and Eyring (1968) suggested that B-type Am₂O₃ was likely to have the same structure as a B-type rare earth sesquioxide.

1.1.1. $Ce^{IV}_{1-x}Nd^{III}_xO_{2-(x/2)}$: A Surrogate for a single phase between $AmO_{1.65}$ and $AmO_{1.75}$

In this study, it is assumed that $AmO_{2-(x/2)}$ can be described as a solid solution between the $AmO_{1.5}$ and AmO_2 end-species, even though Thiriet and Konings (2003) stated that $Am_{5/4}O_2-AmO_2$ may also be valid. The $AmO_{2-(x/2)}$ crystal structure can be described by the replacement of Am^{4+} ions in the AmO_2 crystal with Am^{3+} ions, where half of an oxygen vacancy is introduced each time to ensure charge conservation (Casalta, 1996). This has been described by $Am^{IV}_{1-x}Am^{III}_xO_{2-(x/2)}$, or $AmO_{2-(x/2)}$ for shorthand, where x ranges from 1 ($AmO_{1.5}$) to 0 (AmO_2).

Although there are surrogate materials for AmO_2 and Am_2O_3 , there is nothing similar for the $AmO_{2-(x/2)}$ species. $CeO_{2-(x/2)}$ could be considered; however, these are very difficult materials to handle and readily re-oxidise. Therefore, it would be practical to establish an $MO_{2-(x/2)}$ surrogate material (M designates the metallic part), or a range of materials, that has a stable oxygen-to-metal ratio in air and that has a similar structure to the americium oxide phase of interest i.e. a cubic phase between $AmO_{1.65}$ and $AmO_{1.75}$ here.

Horlait et al. (2011) explained (from information provided by Ikuma et al. (2005)) how the face centred cubic (FCC) CeO_2 structure (Fm-3m), which is called F-type, is doped with neodymium to form a solid solution: the Nd^{3+} ions replace Ce^{4+} ions and half of an oxygen vacancy is produced randomly within the structure for each of these substitutions to conserve charge. The material maintains an F-type structure until, eventually, a sufficient number of substitutions occurs to result in a cubic Ia-3 superstructure (often called C-type), which has a unit cell volume eight times as large as that of the F-type structure. For solid solutions with even larger Nd content, surplus hexagonal Nd_2O_3 is found to be present in addition to the solid solution. Horlait et al. (2011) noted that the synthesis method affects the range of x-values for each crystal phase of the $Ce_{1-x}Nd_xO_{2-(x/2)}$ system at room temperature. The results of their investigation are outlined in Table 5.2. An illustration of the F-type and C-type $Ce_{1-x}Nd_xO_{2-(x/2)}$ unit cells is provided in Appendix C.

Table 5.2: approximate x-ranges for $Ce^{IV}_{1-x}Nd^{III}_xO_{2-(x/2)}$ according to Horlait et al. (2011). Note the exact solubility limits are not stated as only discrete x-values were investigated.

Structure	x-value
F-type	$x \leq 0.39$
C-type	$0.42 \leq x < 0.73$
C -type and A -type Nd_2O_3	$x > 0.73$

A literature review found that an extensive phase diagram of the CeO_2 - Nd_2O_3 system at different elevated temperatures does not exist. The only known phase diagram is presented by Pieczulewski et al. (1990) and comprises only a few data points. Nonetheless, the phase transitions at room temperature are well understood as described in the review by Horlait et al. (2011).

In the context of obtaining a potentially suitable surrogate for a single cubic americium oxide phase between $AmO_{1.65}$ and $AmO_{1.75}$, the oxides between $Ce_{0.3}Nd_{0.7}O_{1.65}$ and $Ce_{0.5}Nd_{0.5}O_{1.75}$ have been considered. According to the AmO_2 - Am_2O_3 phase diagram shown in Figure 5.1 (Thiriet and Konings, 2003), the only single cubic phases that exist between $AmO_{1.65}$ and $AmO_{1.75}$ are either Fm-3m or Ia-3 in structure, which they label as α and C', respectively. As most of the oxides ranging from $Ce_{0.3}Nd_{0.7}O_{1.65}$ to $Ce_{0.5}Nd_{0.5}O_{1.75}$ (x between 0.7 and 0.5) should be Ia-3 (C-type) in structure, some of these could be potential surrogates for these Ia-3 (C') Am oxides. However, as stated earlier, the synthesis method affects the x-value range of the Ia-3 (C-type) phase in the $Ce_{1-x}Nd_xO_{2-(x/2)}$ system and may influence whether surplus A-type Nd_2O_3 may also be produced for $Ce_{1-x}Nd_xO_{2-(x/2)}$ oxides with x-values closer to x 0.7 (Thiriet and Konings, 2003).

The C' Am oxide phase ($AmO_{1.5+\delta}$) is noted in a number of sources but different notations are used. Thiriet and Konings (2003) say its region in the phase diagram is often incorrectly drawn in other studies. Their diagram shows it lies in a region between around $AmO_{1.60}$ and $AmO_{1.69}$ depending on the temperature (these are not the phase boundaries). However, due to limited experimental data, there is some uncertainty in the boundaries

of the phase diagram (see Figure 5.1), as is shown for the C' phase, as well as at low temperatures where data are limited (Besmann, 2010). Thiriet and Konings (2003) provide further details of the phase diagram, as well as a review of past experimental work with Am oxides. Sari and Zamorani (1970) assumed the lower limit of the C' (Ia-3) phase to be around $\text{AmO}_{1.62}$ with an upper limit of $\text{AmO}_{1.68}$. This was estimated based on their differential thermal analyses and XRD data. Nishi et al. (2008) created $\text{AmO}_{1.73 \pm 0.03}$, which comprised two body centred cubic phases with lattice parameters of 10.97 Å and 10.92 Å. Lebreton et al. (2012) conducted a literature review and a detailed in-situ X-ray diffraction study of the Am-O system. They evidenced a C'-type (Ia-3) $\text{Am}_2\text{O}_{3+\Delta}$ phase that had a lattice parameter equal to twice that of Fm-3m $\text{AmO}_{2-\Delta}$ (Lebreton et al., 2012).

Sari and Zamorani (1970) state that the lattice parameter data recorded by Chikalla and Eyring (1968) varied abruptly as O/Am ratio approached $\text{AmO}_{1.67}$. The compositions for which either C or C' (both were inferred to be Ia-3 phases) was the only phase, or the dominant phase, were $\text{AmO}_{1.616}$ through to $\text{AmO}_{1.713}$, which were all made under He at 800/850/860 °C (Chikalla and Eyring, 1968). However, the trend at other temperatures is unknown. If the uncertainties are taken into account, the lattice parameters for this range of oxides existed and varied up and down between 10.889 Å and 11.00 Å (based on the Guinier data of Chikalla and Eyring (1968)) but some were mixed phases. $\text{Ce}_{0.27}\text{Nd}_{0.73}\text{O}_{1.635}$ has a lattice parameter of 11.0536(4) Å, which decreased to 10.9982(26) Å for $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ according to Horlait et al. (2011).

There is the potential for Ia-3 $\text{Ce}^{\text{IV}}_{1-x}\text{Nd}^{\text{III}}_x\text{O}_{2-(x/2)}$ to be a crystallographic surrogate for Ia-3 $\text{AmO}_{2-(x/2)}$ for particular x-values within the 0.5 to 0.7 range. However, the data set for the Am-O phase diagram is limited. Additionally, there are even fewer data for the lattice parameter variations of single C' phases at different temperatures. The behaviour of $\text{Ce}^{\text{IV}}_{1-x}\text{Nd}^{\text{III}}_x\text{O}_{2-(x/2)}$ is not understood at elevated temperatures.

1.2. Study Objectives

The aim of the study reported herein was to demonstrate and evaluate the use of an oxalate precipitation and calcination based process to create $\text{Ce}^{\text{IV}}_{1-x}\text{Nd}^{\text{III}}_x\text{O}_{2-(x/2)}$ as a candidate surrogate for some Ia-3 $\text{AmO}_{2-(x/2)}$ phases. The objectives of this study were to:

1. Understand how varying the temperature of the oxalate precipitation process affects the shape and size of the oxalate particles.
2. Determine whether $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ could be created from the calcination of Ce Nd oxalate co-precipitates, with an expected Ia-3 crystal structure via a continuous oxalate precipitation process.
3. Determine if the $\text{Nd}/[\text{Ce} + \text{Nd}]$ ratio of each oxide is consistent with the nominally chosen x-value, which was selected by the molar ratio of the Nd and Ce nitrate feeds to the precipitator.
4. Assess the reproducibility of the synthesis method by comparing multiple batches of material made in separate repeat experiments using the analysis methods mentioned above. Investigations, such as sintering trials, would require a reproducible surrogate input material.

An x-value of 0.60 was nominally targeted in this study.

Although the production of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system has been explored in the past by solid state routes e.g. by Hong and Virkar (1995), and by wet synthesis routes such as by Higashi et al. (1999) and Horlait et al. (2011), this presented study is the first to have the mixed Ce and Nd nitrates and oxalic acid reagents added (drop-wise) simultaneously into a reaction vessel. Higashi et al. (1999) added a nitrate mixture to oxalic acid to create a different $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ oxide namely, Fm-3m $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$. Although the synthesis of $\text{Ce}_{0.4}\text{Nd}_{0.6}\text{O}_{1.7}$ had been targeted by Horlait et al. (2011) using a wet-synthesis oxalate precipitation route, they reacted a metal chloride mixture with excess oxalic acid and did so by pouring the chloride mixture into the oxalic acid.

Secondly, this is the first known study to have investigated the influence of the oxalate precipitation temperature on Ce Nd oxalate particle properties. It is also the first known investigation to use a method that continuously co-precipitates and filters the Ce Nd oxalates (from the mother liquor) over several hours. It thus offers a simple co-precipitation method.

2. Material Synthesis

2.1. Oxalate Precipitation

A solution comprising Ce(III) nitrate and Nd(III) nitrate with a total lanthanide concentration of 0.0104 M in 0.2 M nitric acid and a 0.68 M oxalic acid solution were fed continuously into a vessel. The reaction vessel was designed to allow continuous co-precipitation of the reaction products and was sat partially within a temperature controlled water bath as illustrated in Figure 5.2. The water was circulated through an integral water jacket on the reaction vessel to ensure uniform temperature. The flow rates of the reagents were controlled by separate calibrated peristaltic pumps. The masses of the raw Ce(III) nitrate hexahydrate and Nd(III) nitrate hexahydrate (99.9%-Ce and 99.9%-Nd, STREM Chemicals UK) were measured under a nitrogen atmosphere to limit water absorption. The masses were measured to ensure a molar ratio of $\text{Nd}/[\text{Ce} + \text{Nd}]$ of 0.6, which was expected to target an x-value of 0.6 in the final oxide (Higashi et al. (1999) mixed their metal nitrates in a 0.2 molar ratio to target the production of $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$). The temperature of the reaction was controlled. The precipitates were continuously filtered through a $0.45\ \mu\text{m}$ Millipore membrane. After several hours of co-precipitation, three vials were used to collect the outflowing precipitate (suspended in the mother liquor) from the vessel outlet (before it reached the filter) for particle size analysis. The filtered material was rinsed with water and dried in an oven at $100\ ^\circ\text{C}$ for a day.

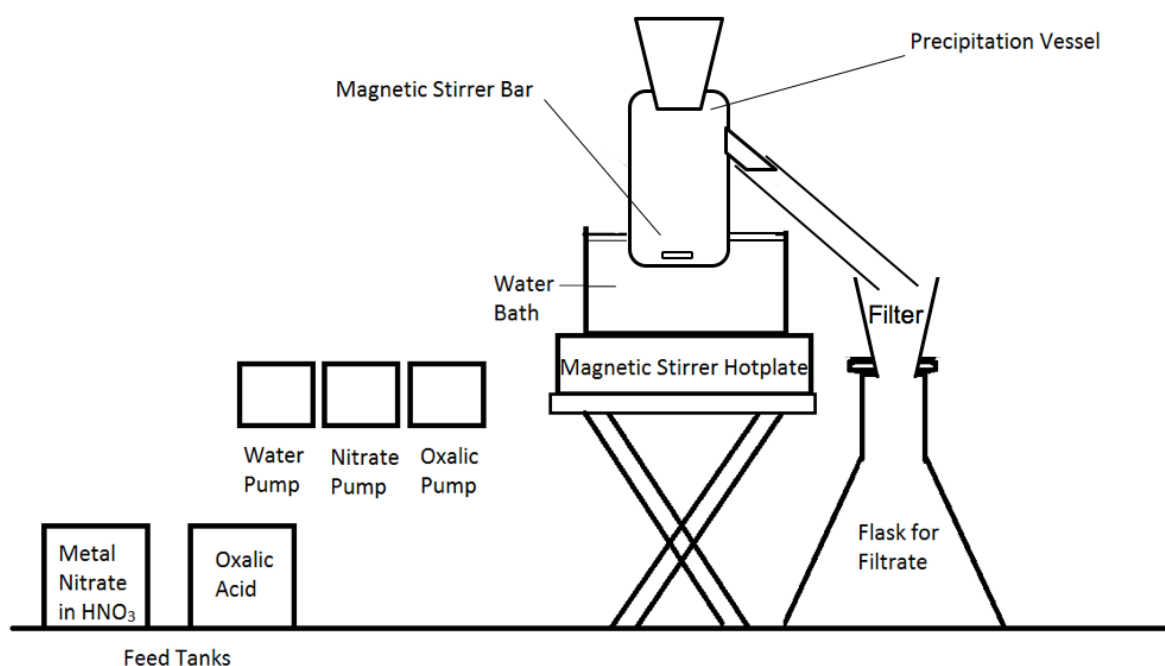


Figure 5.2: A schematic of the oxalate precipitation apparatus.

Samples were precipitated at 25 °C and 60 °C (see Table 5.3). Two investigations were conducted to assess:

1. The effect of reaction temperature on oxalate particle morphology.
2. The effect of reaction temperature on the particle size.

Three experiments were conducted per condition set outlined in Table 5.3 to assess the reproducibility of the method and of the samples. This resulted in three batches of material being made per condition set.

Table 5.3: The oxalate precipitation experimental matrix.

Temperature (°C)	Stirring Rate (RPM)
25	250
60	250

2.2. Calcination

In this study, the dried oxalate precipitates were heated in air in a furnace. The initial heating rate was 5 °C min⁻¹ from 25 °C to 880 °C, which was reduced to 2 °C min⁻¹ up to 900 °C, where it was held for an hour. The former heating rate was chosen for consistency with other literature sources (Horlait et al., 2011, Claparède et al., 2011) and the latter was used to permit gradual heating to the 900 °C target. The cooling process was more gradual and the system was left to cool overnight. Samples were removed from the furnace at around 40 °C. After cooling under ambient conditions for ten minutes, they were stored for subsequent characterisation. There were six calcined oxalate batches in total (three were calcined 25 °C oxalates and three were calcined 60 °C oxalates).

3. Analytical Methods

3.1. Powder X-ray Diffraction (PXRD)

Data were acquired using CuK α radiation in a flat plate (Bragg-Brentano) θ - θ configuration, on a Bruker D8 Advance Powder Diffractometer equipped with a LynxEye Position Sensitive Detector. The ICDD PDF-4+ Scholar database (interfaced with DIFFRAC.EVA) was used for phase identification.

To confirm that the precipitation procedure was producing oxalates, material made in an early trial underwent PXRD. The details of this analysis are outlined in Appendix C.

Two of the 900 °C calcined oxalates underwent PXRD analysis: batch 1 of the 25 °C oxalates and batch 1 of the 60 °C oxalates (see Table 5.3). Diffraction patterns were recorded using the following parameters:

- Scan set a) angular range: 4° to 90° 2 θ ; step size: 0.01° 2 θ ; count time: 0.5 seconds per step.
- Scan set b) angular range: 18 to 52° 2 θ ; step size: 0.01° 2 θ ; count time: 5.0 seconds per step.

The ICDD database and other literature were consulted during phase analysis (Horlait et al., 2011, Ikuma et al., 2005). The time per step was increased in analysis set b in comparison to set a to aid the analysis of low intensity peaks that were indicative of C-type (Ia-3) $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ by improving the signal to noise ratio. According to PDF 04-013-6624, which is the PDF card of C-type $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$, these peaks were the (2 1 1), (4 1 1), (3 3 2) and (1 3 4) peaks.

3.2. Raman Spectroscopy

Data were acquired with a Renishaw Invia Raman microscope under the extended regime. A 50% filter was used to reduce sample heating. Cosmic rays were automatically removed from the data during acquisition. Sections of the samples were stored and transported in glass vials prior to Raman analysis. Each sample was placed, crushed and had its surface flattened in a sample holder. A 10 s dwell time was used and data were acquired over 5 accumulations per sample. Each spectrum was normalised to the maximum recorded intensity and the background was removed. The oxalate precipitates made using the two different temperatures (see Table 5.3) were analysed using a 514 nm He-Ne laser (see Appendix C for details). The three calcined 25 °C oxalate precipitate batches and the three calcined 60 °C oxalate precipitate batches (see Table 5.3) were analysed using a 633 nm wavelength laser to establish if there was evidence of the structure of C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$. One sample was taken from each batch for analysis and multiple locations were analysed. The spectra were acquired at 50x magnification. The ‘laser diameter’ was around 1 μm for the 50x objective. The majority of spectra were the result of averaging over five consecutive acquisitions.

Each data set was normalised and then analysed using LabSpec 5 software (Horiba, version 5.74.29). The background was subtracted (assuming a polynomial of degree 1) using the automatic routine. The peak-fitting tool was used to automatically search for peaks, a Gaussian-Lorentzian profile was assumed and a “Level (%)” of 10% and a “Size(pnt)” of 4 were chosen, respectively for the search. The former parameter was a threshold of the minimum intensity as a percentage of the maximum in the spectrum for peak identification. The “Size(pnt)” referred to the number of data points maxima could be separated by. These first estimates of peak positions were inspected and those that were not clearly evident in the spectra were not considered. The peaks were then fitted using a Levenberg-Marquart fitting procedure. The overall fitted curve and the deconvolved peaks were inspected qualitatively for goodness of fit.

3.3. Quantitative X-ray Fluorescence (XRF)

The calcined oxalate samples underwent quantitative X-ray fluorescence analysis using a PANalytical Axios Advanced X-Ray Fluorescence wavelength-dispersive spectrometer. The data were analysed using the software provided with the instrument (PANalytical SuperQ system with IQ+). Samples were prepared and analysed using the fusion bead method (Jenkins and Vries, 1969c, Jenkins, 1999d). The technique enables repeatable sample preparation by creating homogenous samples that negate mineralogical differences that can affect the measured line intensities. The method used here required 0.1 g of sample per fused bead.

Calibration curves were produced in order to quantify the Ce and Nd ion concentrations in each of the calcined oxalate batches (precipitated at 25 °C and 60 °C according to Table 5.3). Different predefined masses of CeO₂ and Nd₂O₃ were measured to make calibration fusion beads with different wt% of CeO₂ and Nd₂O₃. These were then analysed where the intensities of the isolated Ce L_{α1} (4.8402 KeV) and the Nd L_{β1} (5.7216 KeV) lines were measured and corrected for matrix effects and background. The matrix was stated to be CeO₂ and Nd₂O₃ as the Ce and Nd ions in the fusion melt would have fully oxidised.

Each calcined oxalate precipitate batch (see § 2.2) underwent quantitative XRF analysis to assess the Nd/[Ce+Nd] ratio. Two samples were taken from each batch to make two fusion beads for duplicate analysis, which resulted in twelve beads in total. The beads were analysed as unknown samples where a CeO₂ and Nd₂O₃ matrix was assumed. The software corrected the measured intensities for background, system drift as well as matrix

effects, as described by Jenkins and Vries (1969c) and Jenkins (1999d), and the CeO_2 and Nd_2O_3 concentrations by mass were calculated using the calibration curves. Post-analysis involved converting these to Ce molar % and Nd molar % concentrations (using the atomic weights of Ce, Nd, CeO_2 and Nd_2O_3 according to NIST (2016)) to then calculate the molar ratio $\text{Nd}/[\text{Ce} + \text{Nd}]$. Note an additional factor of two was used to calculate the Nd molar % to account for there being two Nd atoms per Nd_2O_3 .

3.4. Scanning Electron Microscopy (SEM)

Oxalate samples were removed from each dry oxalate precipitate, gold coated and then analysed using a Philips XL30 environmental scanning electron microscope (ESEM) under vacuum. Samples were analysed using the secondary electron mode.

3.5. Particle Size Analysis

The particle size distributions (including Polarization Intensity Differential Scattering, PIDS) of the Ce Nd oxalate suspensions were analysed using a Beckman LS Coulter 230 with the Variable Speed Fluid Module Plus. A 90 s background signal measurement was taken prior to the start of the sequential data measurements and data were acquired for 60 s per measurement.

Three batches of material were made (see § 2.1) using a 25 °C precipitation temperature and another three were made at 60 °C (see Table 5.3). Three vials of suspended precipitates were collected per batch made (see section § 2.1). These suspensions were deemed representative of the oxalates made throughout the synthesis process e.g. hours before, as the experimental conditions (mixing rate and temperature) were maintained for the duration of the precipitation. Each vial underwent particle size analysis. Consequently 9 sets of data were acquired for precipitates made at 25 °C and another 9 for precipitates made at 60 °C. The samples made at 60 °C were analysed first and data sets 1-3 were used to validate the material re-suspension method (vial flipping). A pipette was used to collect suspended material for analysis. Data sets 4-5 were used to establish the time needed for the samples to circulate around the system. The particle size distribution (PSD) of data set 5 shifted relatively little after 30 sequential measurements of the circulating suspension. Hence, the PSD of the 30th measurement of this sample and of each of the remaining 13 vials were compared. Although only five 60 °C oxalate vials were analysed, this was deemed a sufficient number for comparison with the nine 25 °C samples. The

objective of this study was to measure the size distribution of particles in suspension and to determine if any observed trends were consistent with ESEM observations.

The apparatus used a 750 nm light source to analyse particles with equivalent spherical diameters between 0.04 μm and 2000 μm (Beckman Coulter, 2011). Under the PIDS regime, it used three polarised light sources (with 450 nm, 600 nm and 900 nm wavelengths) to analyse particles with diameters between 0.04 μm to 0.4 μm . The SEM analyses outlined in § 4.2.1 indicated that the filtered Ce-Nd oxalate particles typically had dimensions between 1 and 50 μm . Consequently, as the particle diameters were not much greater than the wavelength of the incident radiation (NIST et al., 2001), a Fraunhofer approximation based optical model was discounted and a model based on Mie theory was chosen. This required the real and imaginary components of the refractive indices of the material to be specified as well as that of the suspension fluid. The default value for water (1.332) was specified for the latter.

Due to a lack of data on the refractive indices of Ce Nd (III) oxalates, optical models were specified according to the refractive indices of hydrated Ce(III) oxalate measured by Wylie (1947): 1.47(5), 1.55, and 1.61 for α , β , and γ , respectively. As the model required a single input for the real refractive index, the maximum and minimum of these values were used: ‘Ce Oxalate Max’ assumed a real refractive index of 1.61 and ‘Ce Oxalate Min’ assumed a real refractive index of 1.47. Wylie (1947) did not specify the wavelength of the radiation used to calculate these indices nor their imaginary components. Ideally a refractive index obtained using a similar wavelength to that of the LS Coulter 230 should have been specified.

Generally, it is well known that the definition of the optical model can have an effect on the resultant PSD (NIST et al., 2001, NPL et al., 2009) and as the refractive index of the Ce Nd oxalates is not known, it was important to understand the influence of using a range of refractive index values. To do this, an optical model based on the refractive index of a nuclear material with a vastly different refractive index to Ce (III) oxalate was used, namely UO_2 , despite its different (cubic) crystal structure. The optical model was denoted as ‘ UO_2 ’ and used 2.42 and 0.015 for the real and imaginary refractive index components, respectively (Omori et al., 1996).

4. Results

4.1. Oxide Material Characterisation

4.1.1. XRF

This synthesis route produced samples with a reproducible Nd/[Ce + Nd] ratio. The average Nd/[Ce + Nd] value of all sample beads was 0.62 to 2 s.f. with a coefficient of variation of around 0.1 %. This result was also independent of whether the calcined samples were created from oxalates that were made at 25 °C or at 60 °C (see Table 5.3), which indicated that the precipitation temperature did not affect the ability to target a specific ratio. The ability to make a surrogate with reproducible composition is essential for establishing a synthesis method where samples may be required for multiple investigations.

The target of 0.6 has been achieved with a ~3% discrepancy for all fused beads. A small deviation is not unforeseen e.g. Horlait et al. (2011) found small deviations between their expected x-values and those of their oxides as determined by energy-dispersive X-ray spectroscopy. They attributed it to measurement uncertainty and the hygroscopic nature of their chlorides. Ce and Nd nitrate hexahydrates are slightly hygroscopic and are thus a potential contributing cause for the discrepancy in this study. Efforts were made to contain the material and to generally open it in dry environments.

Counting statistics in the X-ray detection would be a cause for the uncertainty in the quantification of the Nd₂O₃ and CeO₂ wt%. Considering the calibration fused bead with 64.8 wt% Nd₂O₃, the raw and net (that takes into account matrix effects instrumental drift, background etc.) count rates were both very large and essentially the same at around 1.49×10^5 and 1.46×10^5 counts s⁻¹, respectively and thus would have had comparable counting statistics. The random error in the number of counts is proportional to the square root of the number of counts (Jenkins, 1999b). The net number of counts in 40 s was 5.9×10^6 to 2 s.f., therefore counting statistics would, in these cases, have produced very small errors that could not account for the discrepancy in the Nd/[Ce + Nd] ratio.

Following this, as the Nd₂O₃ and CeO₂ used to create the calibration fused beads could have absorbed some moisture due to their slight hygroscopic nature, this could have led to uncertainties in their mass measurements and could have potentially caused

uncertainties in the calibration curves. This thus may have impacted the wt% values determined for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ analysed oxides.

Two beads with approximately 60 wt% Nd_2O_3 and 40% wt CeO_2 (each relative to the total CeO_2 and Nd_2O_3 sample content) were used in the calibration process. These were later measured as unknowns when the oxide samples made in this study were analysed. The accuracy of determining the Ce and Nd concentrations in the calibration beads when analysed as unknowns was assessed. The maximum error was around 1.3 % in the ~ 60 wt% Nd_2O_3 beads and around 0.5 wt% in the CeO_2 beads. It is fair to assume that the uncertainty in CeO_2 and Nd_2O_3 compositions of the oxide samples made in this study are of similar magnitude given their similar composition. Thus, the uncertainty associated with the analytical technique will have also been a contributing factor to the 0.02 discrepancy from the expected $\text{Nd}/[\text{Ce} + \text{Nd}]$ ratio.

Ce and Nd oxalate solubility data in the literature were consulted to understand whether differences in solubility could have also been a contributing factor to the discrepancy in the expected and determined $\text{Nd}/[\text{Ce} + \text{Nd}]$ ratio. According to Rudisill (1999), Nd oxalate is slightly less soluble than Ce oxalate in 0.63 M nitric acid and 0.3 M excess oxalic acid ($45 \mu\text{g ml}^{-1}$ and $51 \mu\text{g ml}^{-1}$ respectively). Assuming that the solubilities are similar for the conditions of this experiment, it is possible that the lower solubility of Nd oxalate compared to Ce oxalate could have been a contributing factor to the 0.02 discrepancy in the expected and measured $\text{Nd}/[\text{Ce} + \text{Nd}]$ ratio.

This quantitative XRF analysis was unable to quantify the presence of oxygen. Powder X-ray diffraction and Raman spectroscopy were used to establish whether the calcined materials had structures consistent with a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ structure and, hence, to permit the inference that the $\text{Nd}/[\text{Ce} + \text{Nd}]$ ratio corresponded to an x-value.

4.1.2. PXRD

The PXRD patterns of the 900 °C calcined 25 °C and 60 °C oxalates are shown in Figure 5.3.

The literature indicated that CeO_2 and F-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ (of low x) have Fm-3m structures (§ 1.2.1) and that their PXRD patterns have similar peak positions, yet they shift relative to those of CeO_2 (to lower 2θ values) for the F-type solid solution with an increase in x-value (Horlait et al., 2011, Ikuma et al., 2005). Thus the lattice parameter of

the system should increase with an increase in x (Horlait et al., 2011, Ikuma et al., 2005). C-type (Ia-3) $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ oxides also have these peaks, and exhibit similar peak shift, but they have additional low intensity peaks, as mentioned in § 3.1.

The PXRD patterns of the calcined 25 °C and 60 °C material had similar peak positions as shown in Figure 5.3. As the positions of the starred peaks were shifted relative to those of CeO_2 (to lower 2θ values), there was no evidence of CeO_2 in either sample. This is illustrated in Figures 5.3b and 5.3c where PDF 00-004-0593 corresponds to CeO_2 . The starred peaks had comparable positions to those of $\text{CeO}_{1.53}$ (PDF 04-006-4613) and $\text{CeO}_{1.8}$ (PDF 04-003-6949) that were both Fm-3m in space group. However, neither option was considered a likely oxide constituent as the experimental conditions precluded it.

In addition to the main peaks (starred), low intensity peaks (not indicated by stars) were present in the PXRD patterns as shown in Figure 5.3a. Together, the main and low intensity were indicative of an Ia-3 structured material. Figure 5.3b illustrates that the low intensity peaks had an improved signal-to-noise ratio when a longer counting time was used (achieved by using scan set b described in § 3.1) compared to those Figure 5.3a. The patterns showed no evidence of Ia-3 Nd_2O_3 (comparisons were made with PDF 04-015-1516 and PDF 04-004-8883) as shown in Figure 5.4a. However, the patterns had similar peak positions, yet shifted to lower 2θ values, to Ia-3 (C-type) $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ (stated as $\text{CeNdO}_{3.5}$, PDF 04-013-6624) as shown in Figure 5.4b. Thus, the PXRD data showed that each calcined 25 °C and 60 °C material was consistent with a C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ solid solution. Finally, there was no evidence of A-type Nd_2O_3 .

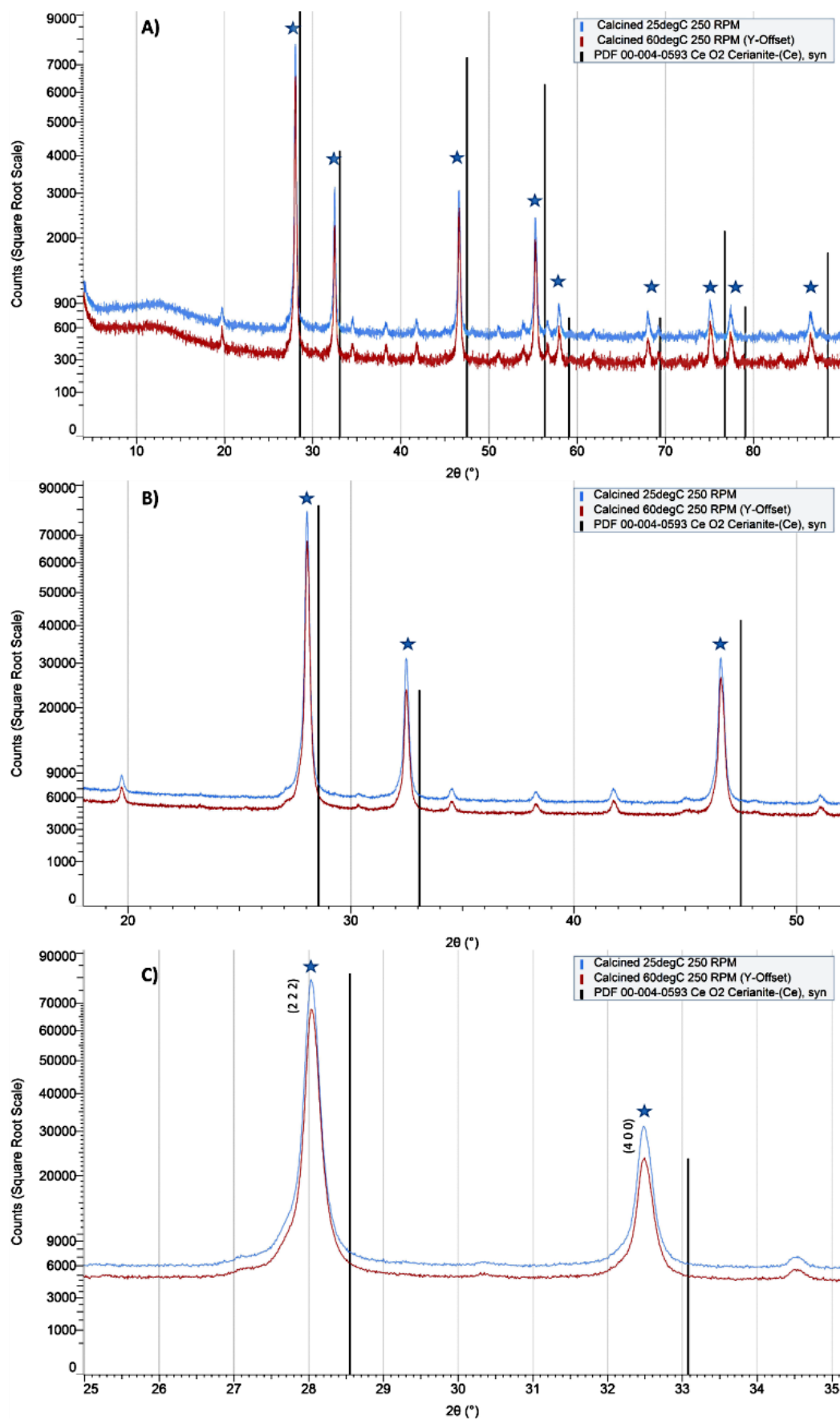


Figure 5.3: Powder X-ray diffraction patterns of the first 900 °C calcined 25 °C (blue) and 60 °C oxalate (red) precipitates (see Table 5.3). A): used scan set a; B): used scan set b and C): used scan set b but illustrates a narrower 2θ range, to illustrate peak shift relative to CeO_2 . Stars indicate the peaks common to CeO_2 and all $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ solid solutions. The calcined 60 °C oxalate XRD patterns have been offset vertically to improve clarity. PDF cards are illustrated. Their intensities have been increased to aid comparisons of peak positions only.

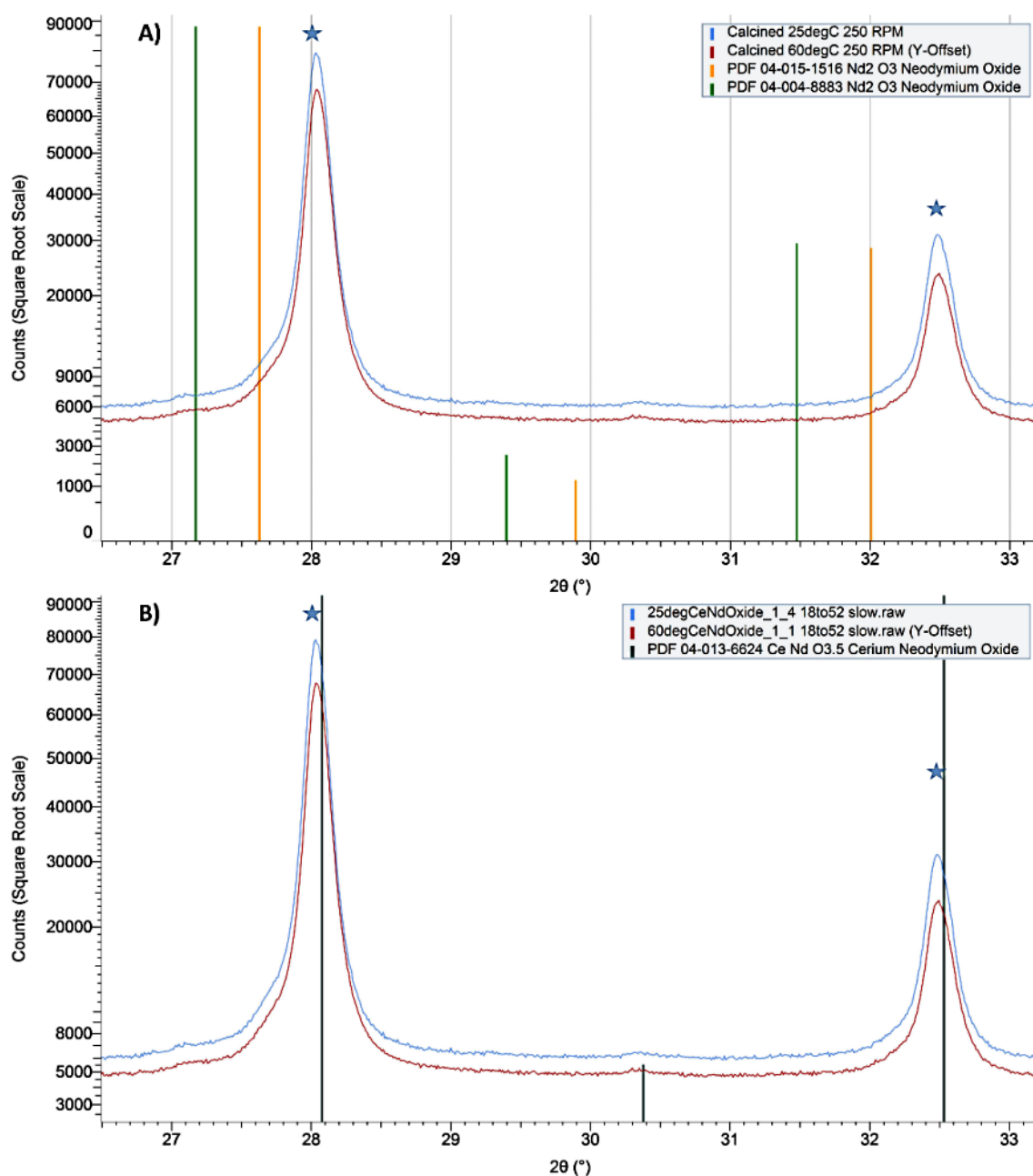


Figure 5.4: Powder X-ray diffraction patterns of the first 900 °C calcined 25 °C (blue) and 60 °C oxalate (red) precipitates (see Table 5.3) collected under scan set b. A): illustrates the peaks do not match with Ia-3 Nd₂O₃ (both PDF cards are Ia-3) and B): shows the peaks had similar positions, yet shifted to lower 2 θ , to Ia-3 CeNdO_{3.5}, which is a C-type Ce_{1-x}Nd_xO_{2-(x/2)} solid solution. Stars indicate the peaks common to CeO₂ and all Ce_{1-x}Nd_xO_{2-(x/2)} solid solutions. The calcined 60 °C oxalate XRD patterns have been offset vertically to improve clarity. The intensities of the PDF cards were increased to aid comparisons of peak positions only.

Gaussian curves were fitted using IDL (see the acknowledgements for further details) to the (2 2 2) and (4 0 0) peaks of the PXRD patterns illustrated in Figure 5.3 to estimate their peak positions. Examples of the fits can be found in Appendix C. These values were then used to provide first estimates of the lattice parameters of the calcined 25 °C and 60 °C oxalates. These particular peaks were chosen due to their large signal-to-noise ratios and because they could be fitted more easily as they did not exhibit noticeable $K\alpha_{1,2}$ splitting. The standard deviations of the fitted Gaussians were calculated from the estimated full widths at half maxima to estimate the uncertainties in the peak positions and, hence, lattice parameters. The averages of the lattice parameter estimates of the oxides made by the calcination of the 25 °C and 60 °C oxalates were both 5.51 Å. The uncertainties in these values were of the order of +/- 0.01 Å.

Equation 1 gives the relationship developed by Horlait et al. (2011) (based on work by Bevan and Kordis (1964)) that related the lattice parameter, a , of single phase ($x < 0.73$) Ce_{1-x}Nd_xO_{2-(x/2)} to x ,

$$a = -5.366 (R_{i\text{Ce}}(1 - x) + R_{i\text{Nd}}x)^2 + 12.10 (R_{i\text{Ce}}(1 - x) + R_{i\text{Nd}}x) - 1.281, \quad (1)$$

where $R_{i\text{Ce}}$ and $R_{i\text{Nd}}$ were the ionic radii of Ce and Nd, which were assumed to be 0.97 Å and 1.109 Å, respectively according to Horlait et al. (2011). This equation predicted that the lattice parameter of Ce_{1-x}Nd_xO_{2-x/2} with x equal to 0.62, which should have a C-type structure, should be 5.51 Å to 3 s.f. This was consistent with the lattice parameter estimates of the oxides in spite of their large uncertainties.

4.1.3. Raman Spectroscopy

The varying blue line in Figure 5.5 illustrates an example of a Raman spectrum at one of the locations of one of the calcined 25 °C oxalate precipitates. The spectra of all samples had very similar profiles in the spectral range of interest (100 cm^{-1} to 750 cm^{-1}). All had main bands around ~ 190 , ~ 260 , ~ 360 , ~ 460 and $\sim 590\text{ cm}^{-1}$ (to 2 s.f.) but the $\sim 530\text{ cm}^{-1}$ peak was not always well fitted. Estimates of the uncertainties in the resultant peak positions were made by inspection by comparing the fitted curves with the data. A conservative uncertainty in the peak positions of $\pm 10\text{ cm}^{-1}$ was assumed for all identified peaks, with the exception of $\pm 5\text{ cm}^{-1}$ for the ~ 460 and $\sim 590\text{ cm}^{-1}$ peaks.

Horlait et al. (2011) provided a literature review of past Raman spectroscopy analysis of CeO_2 and $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-(x/2)}$ solid solutions (Ln refers to lanthanides). The following discussion refers to some of its key points as well as studies conducted by others.

The literature indicated that CeO_2 (Cui and Hope, 2015, McBride et al., 1994), F-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ (Horlait et al., 2011) and C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ (Horlait et al., 2011) all have Raman peaks at around $\sim 465\text{ cm}^{-1}$. For example, Cui and Hope (2015) observed this band in Raman spectra of CeO_2 with a variety of excitation lasers including a 632.8 nm He-Ne laser. This band was assigned to the F_{2g} vibration mode, which describes the symmetric stretching of oxygen ions about Ce metal centres (Horlait et al., 2011, McBride et al., 1994). The Raman band position for CeO_2 could also be affected by particle size (Weber et al., 1993, Graham et al., 1991).

Regarding solid solutions, Horlait et al. (2011) found the F_{2g} position to change from 461 cm^{-1} to 453 cm^{-1} for CeO_2 through to $\text{Ce}_{0.61}\text{Nd}_{0.39}\text{O}_{1.805}$, and they found that there was a shift in band position when the solid solution changed from F-type to C-type. Beyond this shift, there was, again, a decrease in wavenumber with increased Nd content from 466 cm^{-1} to 452 cm^{-1} for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with x equal to 0.42 and 0.785, respectively (the latter showed evidence of additional A-type Nd_2O_3 being present too). Other Raman bands in the recorded spectrum needed to be inspected to ascertain if there was evidence for a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ solid solution.

The Raman spectra of all calcined oxalates indicated the presence of a Ce Nd oxide solid solution by the $\sim 590\text{ cm}^{-1}$ band; McBride et al. (1994), who used a Ar^+ ion laser, found their $\text{Ce}_{1-x}\text{RE}_x\text{O}_{2-y}$ materials (including RE of Nd) to have a band near 570 cm^{-1} in their

Raman spectra. Dohčević-Mitrović et al. (2007), who used a 514.5 nm Ar⁺ laser, found peaks around 600 cm⁻¹ and 550 cm⁻¹ in their Raman spectra of Ce_{0.75}Nd_{0.25}O_{2-δ} solid solutions, which they assigned to oxygen vacancies in their CeO₂ and resulting from the solid solution mechanism, respectively. Horlait et al. (2011) used a 633 nm laser and found the Raman spectra of their solid solutions to have peaks near 580 cm⁻¹, which they associated with oxygen vacancies around metal ions for the A_{1g} and F_{2g} modes of M-O bonds. They found this peak was always accompanied by a ~275 cm⁻¹ peak (the uncertainties in these values were not reported). Thus the ~590 cm⁻¹ and ~260 cm⁻¹ peaks present in the spectra of the current study (Table 5.4) were consistent with a Ce_{1-x}Nd_xO_{2-(x/2)} solid solution.

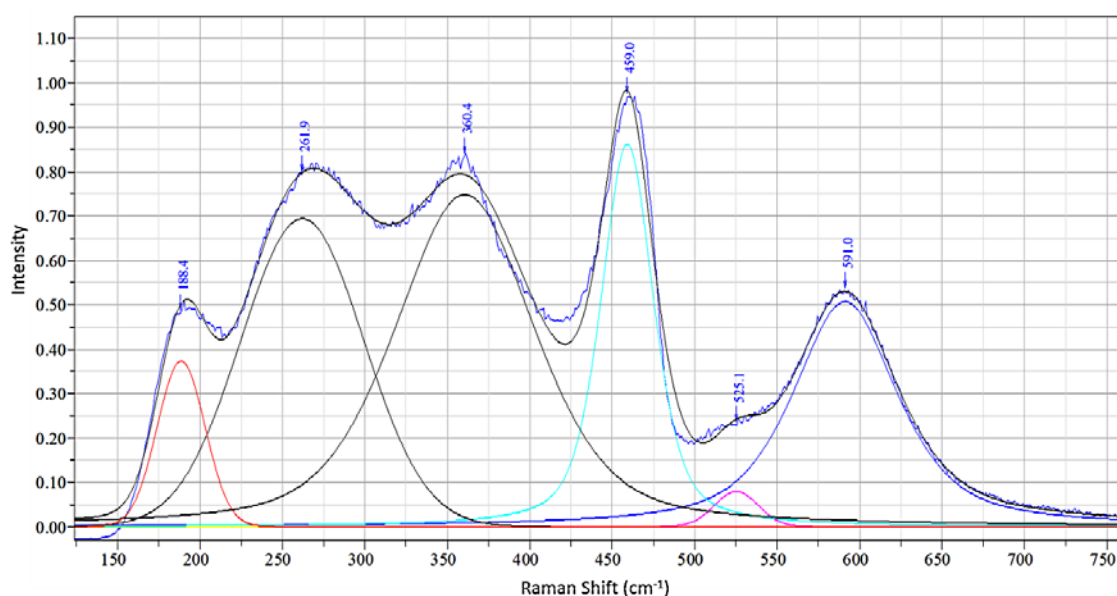


Figure 5.5: The varying blue line is a background removed and normalised Raman spectrum of the second calcined 25 °C oxalate precipitate (see Table 5.3). The spectrum is illustrated between 100 and 750 cm⁻¹. It was one of the better fitted spectra, with the overall fit illustrated in black. The χ^2 value of the fit was 0.0002 to 4 s.f. The deconvoluted curves are shown. Any lines that did not evidence a peak are associated with fitting other areas of the graph e.g. beyond 750 cm⁻¹, such as regions associated with water.

Table 5.4: The estimated peak positions of oxide sample spectra that were reasonably well fitted. N/A signifies that it was not fitted. Conservative uncertainties of $\pm 10 \text{ cm}^{-1}$ are assumed for all peaks except ~ 459 and $\sim 590 \text{ cm}^{-1}$, where $\pm 5 \text{ cm}^{-1}$ is assumed.

Sample ID	Peak Positions (cm^{-1} to 3 s.f.)					
Calcined 25°C oxalate #1 Location 3	188	262	361	459	N/A	590
Calcined 25°C oxalate #2 Location 2	188	262	360	459	525	591
Calcined 25°C oxalate #3 Location 1	189	263	362	459	536	593
Calcined 60°C oxalate #3 Location 1	188	264	362	459	527	591
Calcined 60°C oxalate #1 Location 2	189	262	361	459	527	592

The peak at $\sim 360 \text{ cm}^{-1}$ (see Table 5.4) in all spectra were indicative of an Ia-3 structure. Horlait et al. (2011) noted the presence of a 370 cm^{-1} band and that although it is often associated with C-type (Ia-3) Ln_2O_3 , their XRD data suggested their materials were solid solutions. They thus associated their 370 cm^{-1} peak with the C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ structure. Similarly, the PXRD analysis in this study (§ 4.1.2) negated the likelihood of C-type Nd_2O_3 . Thus the $\sim 360 \text{ cm}^{-1}$ peak in each spectra was ascribed to the presence of a C-type solid solution in each sample.

A small potential peak at $\sim 530 \text{ cm}^{-1}$ was also seen in the collected spectra as shown in Figure 5.5. This was consistent with the “broad shoulder” found in the Raman spectra of the C-type Ce Nd oxide solid solutions in the results of Horlait et al. (2011). The cause for this feature was unknown. The cause for the $\sim 190 \text{ cm}^{-1}$ is yet to be assigned.

Ubaladini and Carnasciali (2008) analysed C-type Nd_2O_3 using Raman spectroscopy with a 633 nm He-Ne laser and found a large peak present at approximately 332 cm^{-1} with the presence of other smaller peaks e.g. between 425 and 450 cm^{-1} . However, Horlait et al. (2011) associated a $\sim 330\text{ cm}^{-1}$ peak, as well as peaks at $\sim 430\text{ cm}^{-1}$ $\sim 480\text{ cm}^{-1}$, with A-type Nd_2O_3 . As there were no clear peaks at $\sim 330\text{ cm}^{-1}$ nor between 400 and 450 cm^{-1} , it was unlikely that Nd_2O_3 was present in either a C-type or A-type form. This corroborated with the PXRD results in § 4.1.2.

The limited Raman spectroscopy studies of Am oxides have resulted in some uncertainties in the collected $\text{AmO}_{2-(x/2)}$ ($\text{Am}_2\text{O}_{3+\delta}$) spectra (Horlait et al., 2014, Naji et al., 2015) and thus a comparison with the results in this study were not made. Additionally, it is noted that the Raman spectrometry data of Am oxide studies to date have not been collected with a 633 nm to allow direct data comparisons.

Overall, the Raman spectroscopy analysis corroborated the PXRD analysis by finding evidence of C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ and no evidence of Nd_2O_3 . However, PXRD was needed to negate the presence of CeO_2 .

4.2. The Effect of Oxalate Precipitation Temperature on Oxalate Particle Morphology and Size Distribution

4.2.1. Scanning Electron Microscopy

Figure 5.6 illustrates examples of ESEM images taken of $25\text{ }^\circ\text{C}$ oxalate precipitates. The particles were lath shaped and had a large range of sizes. Qualitatively, the $60\text{ }^\circ\text{C}$ oxalate particles were larger than the $25\text{ }^\circ\text{C}$ precipitates. The SEM analysis also showed evidence of lath shaped $60\text{ }^\circ\text{C}$ oxalate particles. The $60\text{ }^\circ\text{C}$ samples exhibited charging.

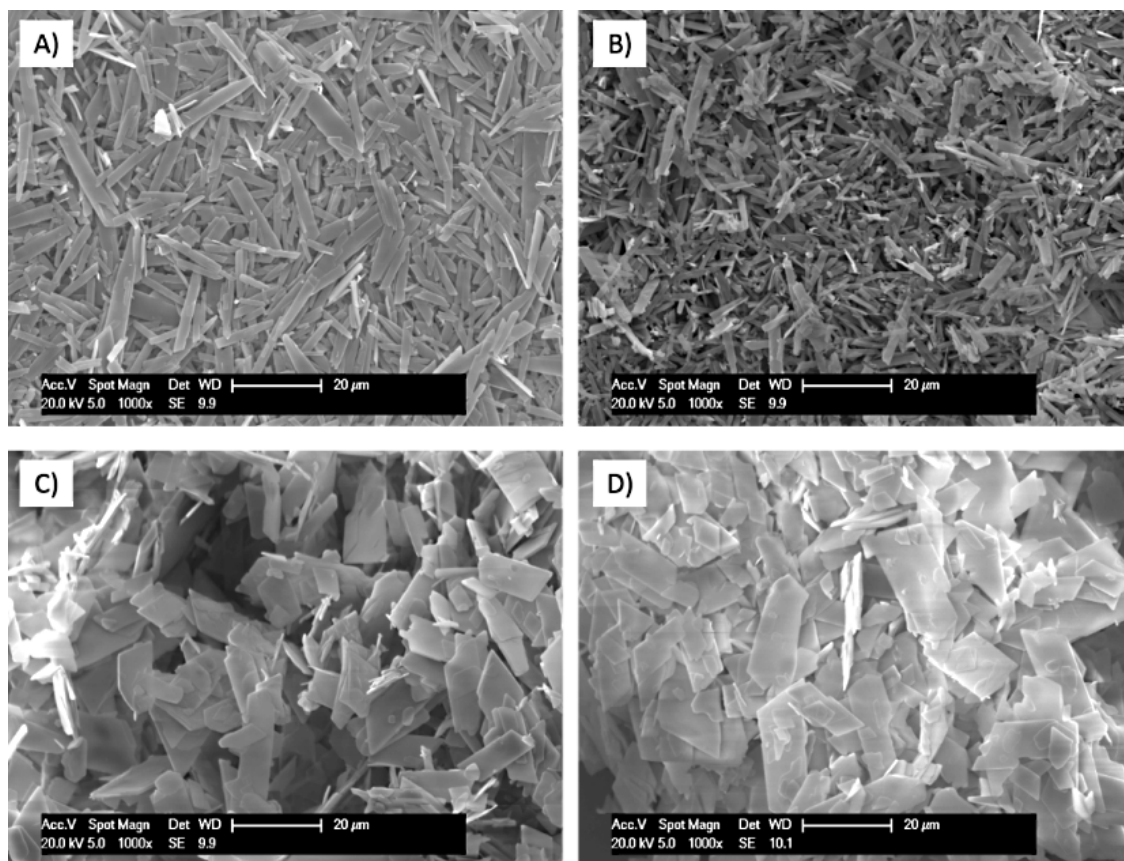


Figure 5.6: Examples of secondary electron (SE) ESEM images of A and B): 25 °C (250 RPM) oxalate precipitates, and of C and D): 60 °C (250 RPM) oxalate precipitates.

A further observation was that the reaction temperature affected how the materials behaved during handling. The 25 °C material remained either intact or was flaky on cutting, but the 60 °C material crumbled easily into a fine powder with a similar consistency to common talc. It is highlighted that these respective macroscopic behaviours were also exhibited by their oxides.

4.2.2. Particle Size Analysis

For brevity, the particle size distributions of the 60 °C and 25 °C precipitated oxalates determined using only two of the optical models are illustrated: the Ce Oxalate Max and UO_2 (see Figure 5.7). The mode values are indicated by the positions of the maximum intensity peaks of each distribution.

The exact values of the particle size distributions depicted in Figure 5.7 are only an approximation of the PSDs due to the assumptions used to process the data, namely, the refractive indices and that the particles were spherical. The trends of the particle size

distributions give a general indication of what would be expected under the sample production conditions used. The analytical method could only be used for the purposes of determining whether the precipitation conditions generated relatively distinct particle size distributions, owing to the assumptions used.

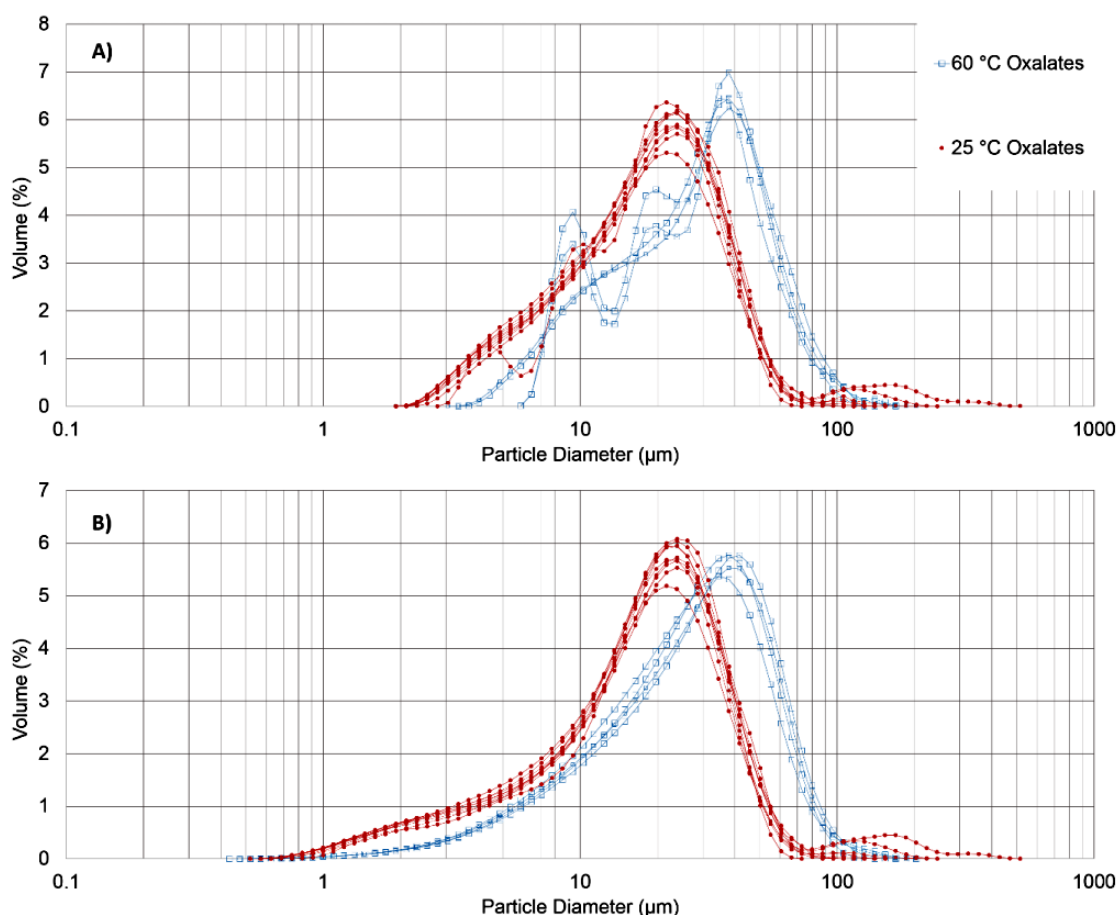


Figure 5.7: A) The 25 °C and 60 °C Ce Nd oxalate particle size distributions (differential volume %) determined using the Ce Oxalate Min optical model and B) using the UO₂ optical model. It shows that the optical modal affects the shapes of the distributions. Regardless of the model, the 60 °C oxalates have larger modal sizes than the 25 °C oxalates. Particle size distributions of different sample vials of 25 °C oxalates are shown but are represented with one colour/symbol and similarly for the 60 °C oxalates, to aid the comparison between the 25 °C and 60 °C oxalates.

Table 5.5 shows that the median particle sizes (d_{50}) of the 25 °C Ce Nd oxalates were smaller than those of 60 °C Ce Nd oxalates by around 10 μm . Figure 5.7 shows there were two distinct sets of PSDs that were resolvable with respect to precipitation temperature. The particles size distributions were also broad and the 25 °C and 60 °C PSDs overlapped.

It is thus likely that the actual 25 °C oxalate material had a smaller modal particle size than the 60 °C oxalate, but all batches contained particles covering a wide size range. These conclusions were corroborated by the ESEM observations noted in § 4.2.1. The optical model choice was sometimes found to affect the PSD shape for a given sample e.g. by affecting the number of peaks. This can be seen by comparing Figures 5.7a and 5.7b, particularly for the 60 °C oxalate material. Nonetheless, this did not affect the observation that the particle size distributions of the 25 °C and 60 °C oxalate precipitates were resolvable with respect to temperature regardless of the optical model used.

Table 5.5: mean d_{50} values of the suspended Ce Nd Oxalate precipitate vials determined using different optical models, together with their coefficients of variation. All values are stated to two significant figures.

		Optical Model		
		Ce Oxalate Max (d_{50})	Ce Oxalate Min (d_{50})	UO ₂ (d_{50})
60 °C	Mean parameter value	28	29	28
	Standard deviation	1.5	1.7	1.5
	Coefficient of variation (%)	5.2	6.0	5.3
25 °C	Mean parameter value	19	19	18
	Standard deviation	0.8	0.8	0.7
	Coefficient of variation (%)	4.5	4.0	3.9

The production method was able to create material with different median and modal particle sizes without the need for ball-milling, but respirable fines (sub 10- μ m particles) were created using both precipitation temperatures as shown in Figure 5.7. Claparède et al. (2011) found that Ce oxalate agglomerates shrank in size by around 25 % on conversion to CeO₂. It is thus assumed that on conversion, the Ce Nd oxalate particles of this study would shrink. Thus more respirable fines could be produced.

5. Concluding Remarks

The ESA programme has identified the potential need to conduct sintering studies with $\text{AmO}_{2-(x/2)}$ species for $0.5 < x < 0.7$. However, investigations with surrogate oxides are an effective precursor providing some initial insight prior to carrying out specific tests with Am oxides. A hypothesis was that $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ could be used as a mixed metal oxide surrogate for certain $\text{AmO}_{2-(x/2)}$ species and that different oxygen-to-metal ratios (O/M) could be targeted by changing the molar ratio of the Ce and Nd in the metal nitrate feed, as the latter had been possible in a study by Higashi et al. (1999). The theory suggested that only the ratio of the metals in the oxide i.e. $\text{Nd}/[\text{Ce}+\text{Nd}]$, needed to be measured to determine x and hence the O/M ratio.

This study has demonstrated a production route for creating $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a nominal target of x equal to 0.60. A number of analysis procedures have been used and developed to characterise oxide composition and structure as well as oxalate particle characteristics. The oxalate precipitation method enables material to be created continuously with minimal attendance, which would be an advantage for regular production.

Oxalate precipitates were created under a range of conditions to investigate the impact of changing the precipitation temperature on particle shape and size. Those precipitated at 25 °C and 60 °C at 250 RPM were calcined to oxides. Quantitative XRF determined the $\text{Nd}/[\text{Ce}+\text{Nd}]$ ratio of each oxide batch to be 0.62. The production process was thus able to achieve the target to within a small discrepancy and create material with batch-to-batch ratio reproducibility. This a key step in being able to produce a reproducible material as reproducible surrogates would be essential for sintering trials. The results also demonstrated that the ratio was precipitation temperature independent.

Powder X-ray diffraction and Raman spectroscopy analyses showed that the production process created $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with Ia-3 structure without additional Nd_2O_3 . Although the O/M ratio was not measured directly, the fact that the oxides had structures consistent $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ suggested that x -values of 0.62 had been achieved i.e. $\text{Ce}_{0.38}\text{Nd}_{0.62}\text{O}_{1.69}$ had been made. However, the small discrepancy of around 0.02 showed that an x -value can be affected by experimental processes (hygroscopicity and solubility variations). As

the lattice parameter is indicative of the x-value, future work will expand on the XRD analysis of the oxide samples to constrain better the lattice parameter estimate.

The literature review has highlighted that more experimental Am oxide crystallographic data is needed to create a more detailed Am-O phase diagram with greater certainty. This is particularly important to the ESA programme for Am oxide sintering studies. From a surrogate stand point, the greater the knowledge about the Am-O phase diagram there is, then the easier the suitability assessment of different candidate surrogates will be. For this study in particular, more detailed experimental studies are needed for species near $\text{AmO}_{1.69}$. Additionally, high temperature crystallographic data of $\text{Ce}_{0.38}\text{Nd}_{0.62}\text{O}_{1.69}$ would be needed too. Once these data are obtained, then the suitability of $\text{Ce}_{0.38}\text{Nd}_{0.62}\text{O}_{1.69}$ as a crystallographic surrogate can be assessed. However, the indications suggest it is a potential surrogate based on the room temperature knowledge of $\text{Ce}_{0.38}\text{Nd}_{0.62}\text{O}_{1.69}$ and limited data about oxides near $\text{AmO}_{1.69}$, particularly as the C' (Ia-3) phase has a tentative phase boundary in the Am-O phase diagram by Thiriet and Konings (2003) (see Figure 5.1). Future work should also include high temperature XRD investigations with $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ to develop a phase diagram such that other $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ phases can be assessed for surrogate suitability at high temperature.

It has been shown that $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a target x-value can be made easily to within some uncertainty and thus there is the potential to create $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with different x-values readily, if needed. Although the focus is on higher x-values, the literature indicates that $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system with x-values up to around 0.4 is FCC in structure. Thus, there is also the potential to create and use it as a surrogate for FCC $\text{AmO}_{2-(x/2)}$ up to around x equal to 0.4, should this range ever be considered.

This study has shown that the oxalate precipitation temperature can have a noticeable impact on oxalate particle size: those precipitated at 60 °C (at 250RPM) were larger by around 10 µm (median particle size) than the lath shaped particles precipitated at 25 °C (at 250 RPM).

Future work should include characterising the particle size distribution of the resultant oxide batches to assess if the 60 °C material remains larger than the 25 °C. It is essential that efforts are made to ensure that respirable particles do not become airborne to minimise the possibility of damage to personnel health.

Oxide particle size could impact how well materials sinter into discs or pellets, and potentially influence sintered body integrity and mechanical properties. The ability to sinter an integral pellet with integrity and relatively high density is essential to the ESA program. As the physical characteristics such as the shape and size of the oxalate particles are likely to influence those of the subsequent oxides, this study has provided a step forward into producing surrogate oxides of the $\text{MO}_{2-(x/2)}$ form with a range of sizes. Thus if the solid solution is a suitable surrogate, small scale sintering trials should be conducted with $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ powders made from 25 °C and 60 °C (250 RPM stirring rate) oxalates.

6. Acknowledgements

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CHAPTER 6: SINTERING TRIALS OF ANALOGUES OF AMERICIUM OXIDES FOR RADIOISOTOPE POWER SYSTEMS

This chapter is based upon a paper (Watkinson et al., 2017b) published in the Journal of Nuclear Materials. Please see the Publications page.

1. Introduction

The overarching aim of this study was to investigate and demonstrate the sintering of suitable surrogate oxides for americium oxides whilst comparing the performance of the cold-press-and-sinter and spark plasma sintering (SPS) approaches. The requirement was for a reproducible process to produce an intact cylindrical pellet of ~13 mm diameter by ~16 mm long. It was sized assuming a requirement for an RHU generating several watts of thermal power ($\sim 3 \text{ W}_t$). Two main driving constraints were considered. Firstly that the relative density of the material should be 85-90 % of theoretical density (T.D.) to allow helium escape during operation. Secondly, for radiological protection reasons, the powder used for the sintering should not be subject to any ball-milling prior to sintering. This is both to reduce respirable fines and equipment contamination (Borland et al., 2009).

In conventional cold-press-and-sinter, powders are compacted under pressure (typically by using a steel die) at room temperature to improve their packing density to form ‘green’ bodies (Basu and Balani, 2011). The green discs or pellets are then heated in a furnace according to a specified time-temperature cycle to sinter the compact. The sintering dwell time for cold-pressed-and-sintered bodies can be several hours. In spark plasma sintering, the heat is generated by direct Joule heating of conductive dies and the powder if it is sufficiently electrically conductive. This allows high sintered densities to be achieved much more quickly and/or at lower temperatures than conventional methods. It also has the potential to manufacture near-net shaped pellets (Aalund, 2010). Graphite dies are often used and so SPS is described as providing a reducing sintering environment for sintering oxides (Guillon et al., 2014); this is a potential disadvantage compared to the conventional cold-press-and-sinter approach.

Non-radioactive surrogate materials provide early insights into how the fuel will behave without the challenges of working with active material (Watkinson et al., 2017a). Neodymium (III) oxide (Nd_2O_3), cerium (IV) oxide (CeO_2) and solid solution oxides of the two have been identified as appropriate surrogates for Am_2O_3 , AmO_2 and sub-stoichiometric AmO_2 , respectively, based on crystal phases and cationic radii, and on transition temperatures, melting points and thermal expansion coefficients (Watkinson et al., 2017a, Williams et al., 2013, Claparède et al., 2011). The current ESA americium fuel chemical flow-sheet creates AmO_2 particles with lath-shaped morphology of tens of micrometres in size (Sarsfield et al., 2016a). Production of surrogate CeO_2 material using a directly analogous oxalate precipitation and calcination process has also been demonstrated to produce micrometric lath-shaped CeO_2 particles (Sarsfield et al., 2016b).

Cold-press-and-sinter has been successfully demonstrated for nanometric CeO_2 powders (Zhou and Rahaman, 1997, Ozawa, 2004, Wang, 2006, Li et al., 2001, Zhou and Rahaman, 1993, Jahromi, 2009). Near full density was achieved in a number of these studies. Reduction of the ceria, resulting in oxygen outgassing, pore production and reduced relative densities of between 70-85 % T.D. was observed in some studies (Zhou and Rahaman, 1997, Ozawa, 2004, Meriani, 1989). Wang (2006) demonstrated the cold-press-and-sinter of CeO_2 at a larger powder size of 5 μm ; however, this was ball-milled before sintering. Roleček et al. (2017) reported a comparison of cold-press-and-sintered milled and non-milled powder. The relative densities achieved were 72.2 % T.D. to 91.3 % T.D. when non-milled powder was used, and 81.4 % T.D. to 95.4 % T.D. when milled powder was used. Data for particle size and morphology of the powder (in particular whether the powder is lath-shaped) were not reported by Roleček et al. (2017). Cold-press-and-sinter of Nd_2O_3 has been reported (Heintz et al., 1989) using powder with an average grain size of 4 μm , achieving a relative density of 86-89 % T.D. but with cracking attributed to a hygroscopic reaction.

There has been limited research into the SPS of pure or doped CeO_2 . Choi et al. (Choi et al., 2010, Choi et al., 2012) investigated the SPS processing of pure nanometric CeO_2 and achieved greater than 97 % relative density. The aforementioned study by Roleček et al. (2017) was a comparative study on the SPS and cold-press-and-sinter of CeO_2 . They spark plasma sintered milled CeO_2 , which was described previously. SPS allowed a much reduced processing time (5 min *cf* 1 hour) and pressure (50 MPa *cf* 300 MPa). Their XRD

data evidenced CeO_2 reduction to Ce_2O_3 . Mori et al. (2005) also reported difficulties in the densification of doped nano- CeO_2 processed using SPS due to reduction. The SPS of ball-milled Nd_2O_3 powder, which had a nominal particle of size of 4 μm prior to milling, was demonstrated to achieve high relative density of 98.8 % T.D. (Williams et al., 2013).

One of the few mechanical properties reported for actinide oxides and their surrogates is Vickers hardness (Williams et al., 2013, Muta et al., 2013, Ge et al., 2013). This standard technique can be conducted on small samples of material (ASTM C1327 - 08, 2008), and the data obtained allow an initial comparison with collated values of similar materials. Jahromi (2009) measured the Vickers hardness of cold-press-and-sintered CeO_2 using a 0.25 N testing load to be between 4.6 GPa and 7.7 GPa depending on sintering temperature. No open literature reporting Vickers hardness for pure Nd_2O_3 has been found.

The objective of this study was therefore to investigate spark plasma sintering (SPS) and conventional cold-pressing-and-sintering of micrometric CeO_2 and Nd_2O_3 . Wherever practical, these studies would use lath-shaped micrometric CeO_2 produced directly from the wet chemical process that would be applicable to the eventual flight fuel form. In all cases, ball-milling of the powders would be avoided. The study is exploratory with no known public studies on the SPS of such large particulate CeO_2 or on the effect of the lath particle morphology on sintering behaviour.

The development of an SPS process using commercially available micrometric CeO_2 sintered in two stages to manage the reduction and outgassing is reported. These sintering parameters were then used to produce near-net shaped ceria pellets using lath-shaped material. Pellets were also produced using conventional cold-press-and-sinter from lath-shaped material of different particle sizes and specific surface areas. The SPS of commercially available Nd_2O_3 was performed to demonstrate the production of near-net shape pellets and for Vickers hardness measurement.

2. Method

2.1. Materials

Pale yellow commercial CeO₂ powder (99.9 % purity, Sigma Aldrich, UK) with a particle size <5 µm was procured for use in the initial SPS studies. This approach was taken because the wet chemical process for synthesising CeO₂ produces small volumes of material and more material was needed for initial trials. The as-received particles are shown in Figure 6.1a.

Wet-chemically synthesised CeO₂ was prepared via an oxalate precipitation and calcination process. The former used 0.083 M cerium (III) nitrate hexahydrate in 0.2 M nitric acid and 0.68 M oxalic acid. The method is a continuous precipitation process (Sarsfield et al., 2016b) and is similar to a process previously described (Watkinson et al., 2017a). The oxalate precipitation temperature and calcination temperatures used are given in Table 6.1. This process yields lath-shaped particles as shown in Figure 6.1b. A Malvern Mastersizer 3000 was used to conduct the particle size analysis using a wet dispersion technique. It used low angle laser light scattering to obtain particle size distributions. A Micrometrics Tristar2 was used to measure the specific surface area of the powder samples using the Brunauer-Emmett-Teller (BET) method. Table 6.1 shows that the calcination temperature has a significant effect on specific surface area, with a lower calcination temperature resulting in a higher specific surface area. The impact of the precipitation and calcination conditions on particle size was more subtle as shown by Table 6.1.

Commercially sourced neodymium(III) oxide powder (99.9 % purity, Alfa Aesar, UK) was procured for the SPS trials using the same product code as stated in a previous SPS study, which had a particle size of approximately 4 µm (Williams et al., 2013).

Table 6.1: Outlines the wet-chemical synthesis oxalate precipitation and calcination conditions used to make the different batches of lath-shaped CeO₂, together with their sizes and specific surface areas. The material and its measured properties were supplied by the National Nuclear Laboratory in collaboration as part of the study by Watkinson et al. (2017b).

Batch #	Oxalate Precip. Temp. (°C)	Calcination Temp. (°C)	Particle Size (µm)				Specific Surface Area (m ² g ⁻¹)
			d ₁₀	d ₅₀	d ₉₀	Volume Mean	
1	25	500	5	25	68	32	67
2	25	650	6	27	70	33	20
3	25	900	6	27	73	38	2
4	60	500	5	23	78	33	69
5	60	650	4	13	37	17	17
6	60	900	5	20	62	28	4

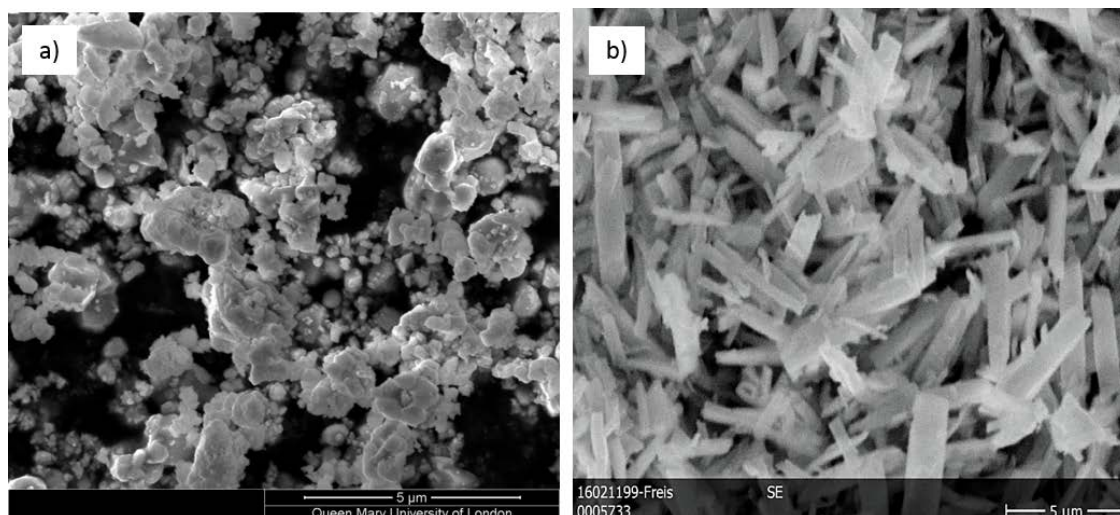


Figure 6.1: SEM images of (a) the as received CeO₂ commercial material and (b) an example of synthesised lath-shaped CeO₂. The latter was provided by the National Nuclear Laboratory in collaboration as part of the study by Watkinson et al. (2017b).

2.2. Sintering Profiles and Methodology

2.2.1. Spark Plasma Sintering of Cerium (IV) Oxide

Initial trials investigated the heating rate, peak temperature, pressure, hold time and the cooling conditions for producing 20 mm diameter disc specimens using a single step sintering profile. The main parameters investigated were the variation of temperature between 1100 °C and 1500 °C and pressures of 50 MPa and 80 MPa. The pressure of gas evolved from the specimen during processing was measured by the SPS furnace. A graphite die (Duragraph 20) was used with graphite paper (Papyex N998) to aid electrical contact.

Sintering profiles A and B, which are illustrated in Figure 6.2, were used to sinter 20 mm diameter discs (A and B) using commercial CeO₂ powder. The first sintering stage in each profile targeted 1050 °C and 1100 °C, respectively, to allow the material to reduce and lose oxygen at a lower relative density. The higher temperatures and pressures of the second stage of each profile were used to consolidate the reduced ceria. The discs were allowed to free cool.

The wet-chemically synthesised lath-shaped CeO₂ from batches 1 and 2 were sintered using sintering profile C, which is illustrated in Figure 6.2, to target the fabrication of cylindrical near-net shaped pellets. A graphite die (Duragraph 465) with an internal diameter of 13 mm was used with a target pellet length of 16 mm. The sintering profile was based on Condition B but featured a more gradual cooling profile (20 °C min⁻¹ from 1300 °C to 450 °C and then to room temperature with no pressure applied) and a lower pressure of 50 MPa. These changes were made with the aim of reducing the risks of failure of the graphite die and pellet cracking due to thermal stresses.

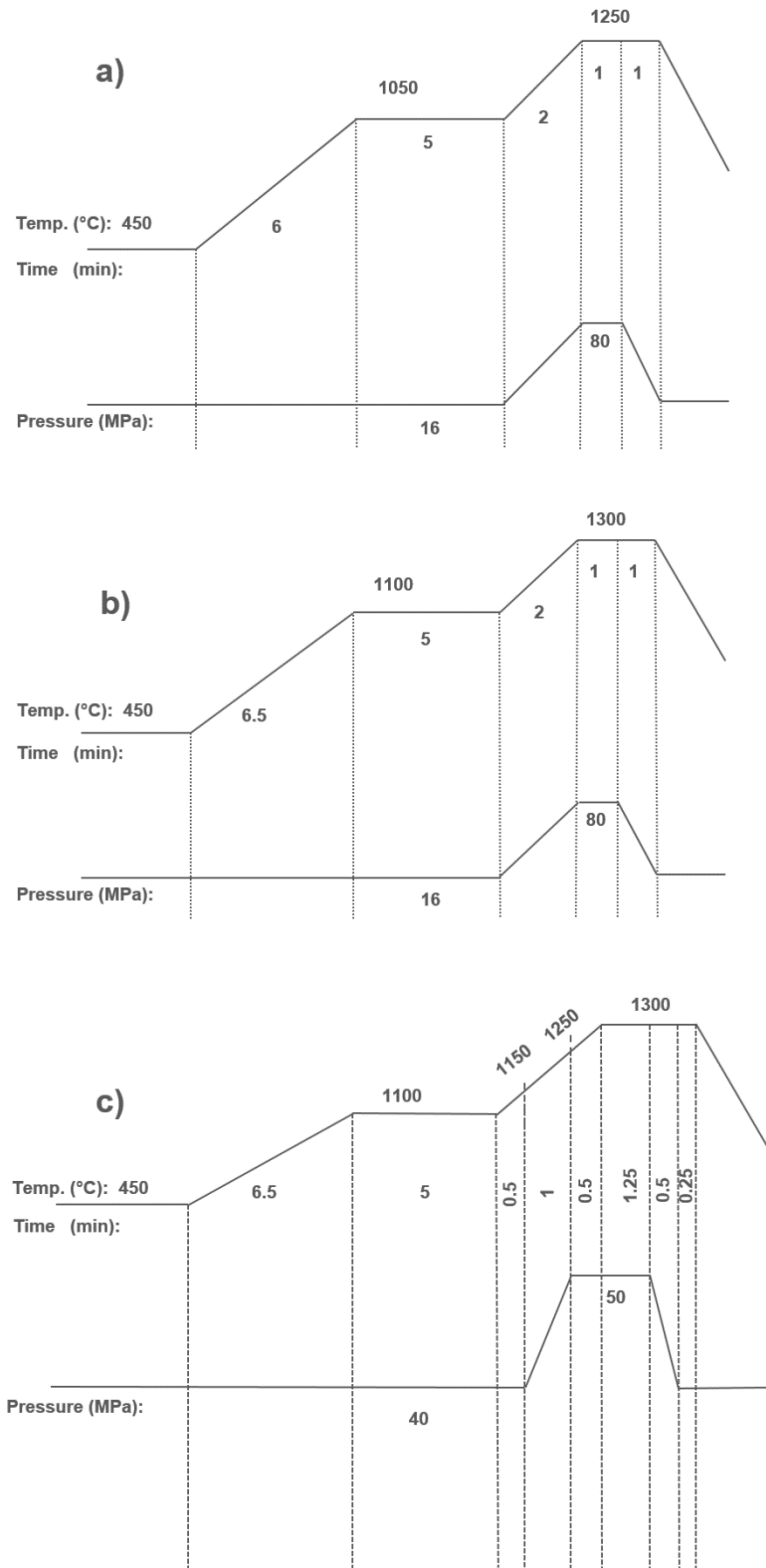


Figure 6.2: SPS sintering profiles used by Queen Mary University of London following discussions. a) Two-stage SPS Condition A used with commercial CeO_2 ; b) Two-stage SPS Condition B used with commercial CeO_2 and c) Two-stage SPS Condition C used with lath-shaped CeO_2 and commercial Nd_2O_3 to produce near-net shape pellets.

2.2.2. Cold-Press-and-Sinter of Cerium (IV) Oxide

Wet chemically synthesised lath-shaped CeO_2 from batches 1-6 (see Table 6.1) were pressed into discs using a 53 kN load and a die with inner dimension of 8 mm. No binder was used. It was not possible to produce intact green discs out of CeO_2 batches 4 and 6. Multiple attempts were made with batch 4. A programmable furnace with MoSi_2 u-pin elements (CM Inc., Bloomfield, NJ) was used to sinter the green bodies. The sintering profile used is shown schematically in Figure 6.3.

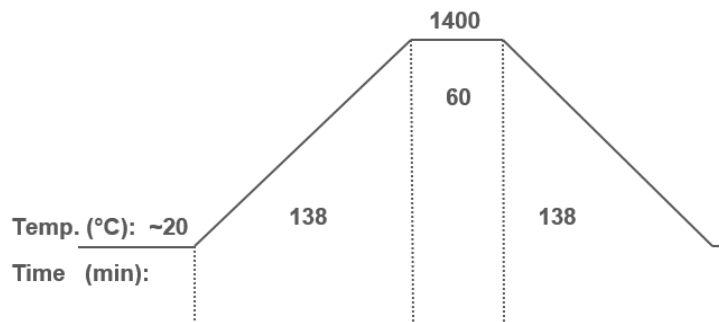


Figure 6.3: The sintering profile used by University of Dayton Research Institute to sinter the cold pressed lath-shaped CeO_2 discs in air as part of the study by Watkinson *et al.* (2017b).

2.2.3. Spark Plasma Sintering of Neodymium (III) Oxide

Sintering profile Condition C, which is depicted in Figure 6.2, was used to demonstrate whether a near-net shaped pellet could be fabricated from commercially procured Nd_2O_3 . Sample dimensions were the same as those for the CeO_2 pellets (section 2.2.1). Condition C was adapted by varying the temperature between 1000 °C and 1350 °C, whilst keeping the pressure at 50 MPa, to identify a suitable temperature to achieve the target relative density of 85-90 % T.D. A further near-net shape pellet was then sintered using the temperature identified by this part of the study to investigate the effect of the aspect ratio on the sintering behaviour.

2.3. Characterisation

The relative densities of the discs and pellets were calculated geometrically, rather than using an Archimedes method, in order to prevent potential degradation of the specimens due to immersion in any liquid. All CeO_2 materials were nominally assumed to have a theoretical density of 7.20 g cm^{-3} . The theoretical density of Nd_2O_3 was taken to be 7.24 g cm^{-3} . A combined uncertainty estimate on the relative density was produced for all

specimens based on measurement precision and on statistical variation where multiple measurements were made of a given dimension. Specimens were stored in sealed vacuum bags in a dry cabinet for between one week and nine months between production, inspection and testing.

Microscope and visual inspection of the specimens was performed to investigate the microstructure and to confirm whether intact pellets could be produced for each material and sintering condition.

Vickers hardness tests were used to assess the mechanical properties of materials produced since this is one of the few mechanical parameters for which literature data for actinide and lanthanide oxides were available.

The specimens needed to be mounted, ground and polished prior to testing. They were cold mounted in epoxy resin with a hardener, ground (using SiC paper of decreasing grit size) and polished with diamond paste on a circular rotating wheel for the SPS samples prepared at UoL and by hand for the cold-pressed-and-sintered samples prepared at UDRI. Water was used as a lubricant for the grinding stage. The final polish was conducted using colloidal silica ($\leq 0.06 \mu\text{m}$). Vickers hardness measurements were performed following ASTM standard C1327-08 (ASTM C1327 - 08, 2008) using a 300 gf load and 15 s dwell time on the prepared specimens at ambient conditions.

The ASTM standard required the acceptability of each Vickers indent to be assessed using its outlined criteria. Ten acceptable indents were used to calculate a mean and standard deviation of the hardness for each test case. The CeO_2 spark plasma sintered discs were mounted such that their fractured surfaces would be polished. The near-net shaped SPS pellet, cold-pressed-and-sintered CeO_2 discs and an Nd_2O_3 disc produced using SPS were mounted with their circular faces upwards.

Vickers hardness tests were performed at University of Leicester (UoL) using a Mitutoyo MVK-G1 Hardness Tester and by colleagues at University of Dayton Research Institute (UDRI) using a Buehler 1600-6300 Vickers hardness tester. This meant the tests were potentially susceptible to subjective differences such as in judging acceptability of indentation morphology and minor differences in procedures such as repeat measurements of individual indentations. For example, scanning electron microscopy (SEM) was used to measure the indents in the CeO_2 SPS discs because material uplift

made it difficult to obtain focussed optical images. For each specimen, this required several indents to be made, the sample to be gold-coated, and then the acceptability of each indent to be assessed using SEM. High resolution images were captured and the indent dimensions were measured offline with standard image analysis software (ImageJ). The SPS 'indented' discs A and B were stored in a dry cabinet for around 8 months before SEM assessment. These differences in Vickers hardness procedures between UoL and UDRI should be considered when comparing the results. However, in this case the objective is to generate indicative data only and so any procedural difference does not place major limitations on the study conclusions.

3. Results

3.1. Cerium (IV) Oxide

3.1.1. *Behaviour of CeO₂ under Spark Plasma Sintering*

The results of the one-stage initial SPS sintering trials using commercially sourced CeO₂ (§ 2.2.1) are shown in Table 6.2. The discs cracked on removal from the die. Visual observation of the discs revealed they were generally grey rather than pale yellow, which was the colour of the powder prior to sintering.

The results in Table 6.2 show that a small change in parameters can have a large effect on the relative density of the disc. Achieving the required relative density range of 85-90 % T.D. can be readily achieved by selecting the appropriate conditions. Figure 6.4 illustrates the fractured surfaces of some of the produced discs. It qualitatively illustrates that an increase in temperature improved consolidation. The impact of increasing the temperature from 1200 °C to 1300 °C under an 80 MPa pressure for 3 min resulted in grain growth. Increasing the sintering temperature to 1500 °C resulted in a significant change in fracture surface microstructure. This is illustrated in Figure 6.5, which is at a higher magnification than Figure 6.4. The sintering is improved in the 1500 °C disc; however, its angular surfaces suggest grain pull-out and non-optimal consolidation. Figure 6.6 shows that outgassing was detected in one of the early trial discs as the temperature passed 1025 °C.

Table 6.2: The parameters used for single-stage SPS using commercially sourced CeO₂. Performed by Queen Mary University of London (QMUL) following discussions. For clarity, only the uncertainty in the relative density is stated.

Temp. (°C)	Pressure (MPa)	Time (min)	Mass (g) ± 0.1 g	Diam. (mm) ± 0.1 mm	Thickness (mm) ± 0.1 mm	Sintered Density (g cm ⁻³)	% Theoretical Density (T.D.)	SPS Machine Left to Free Cool at high temperature? (Yes/No)
1100	50	3	7.2	20	4.3	5.3	74 ± 1.4	No
1250	50	3	7.2	20	3.8	6.0	84 ± 1.7	Yes
1200	80	0	7.2	20	4.5	5.1	71 ± 1.3	No
1200	80	3	7.2	20	3.9	5.9	82 ± 1.6	No
1300	80	3	7.2	20	3.6	6.4	88 ± 1.9	No
1500	80	3	7.2	20	3.5	6.5	91 ± 2.0	No

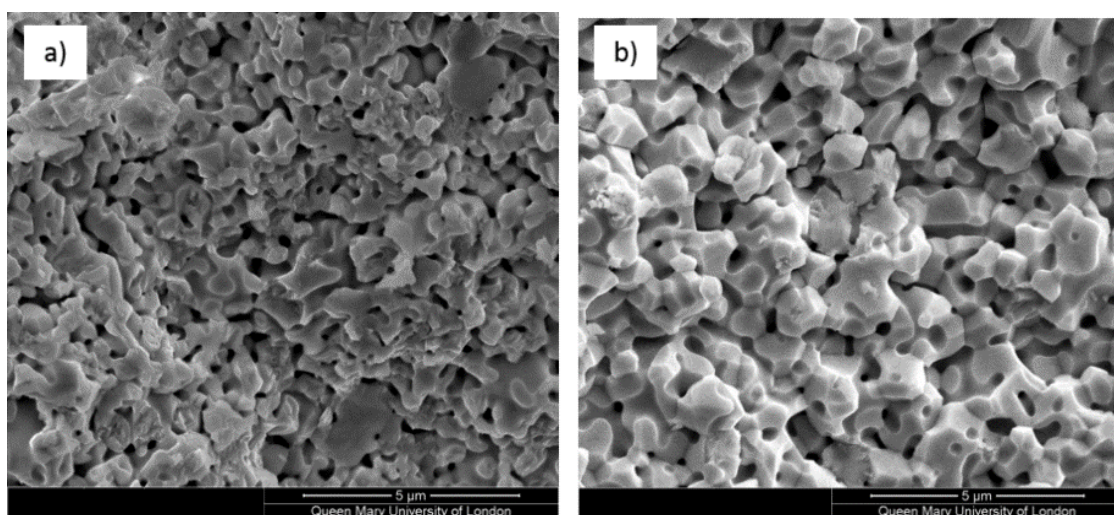


Figure 6.4: The microstructures (5 µm scale) of some of the single-stage SPS ceria made under the following conditions: a) 1200 °C/80 MPa/3 min and b) 1300 °C/80 MPa/3 min using commercially sourced CeO₂. Recorded by Queen Mary University of London as part of the collaboration study by Watkinson et al. (2017b).

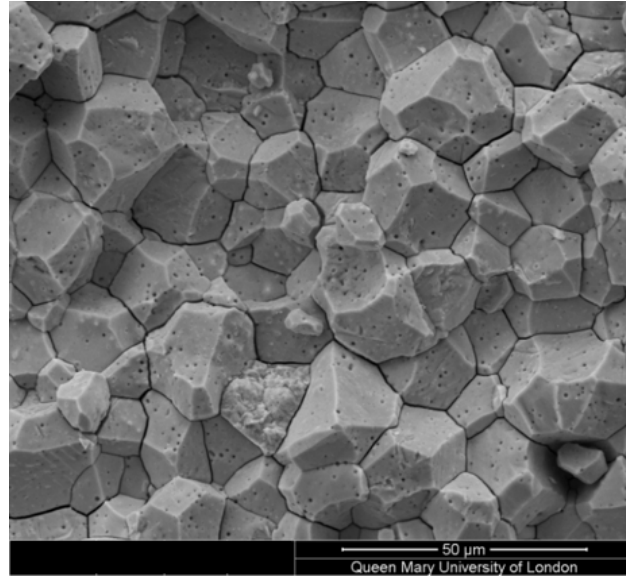


Figure 6.5: The microstructure of a single-stage SPS disc made at 1500 °C/80 MPa/3 min using commercially sourced CeO₂. Recorded by Queen Mary University of London as part of the collaboration study by Watkinson et al. (2017b).

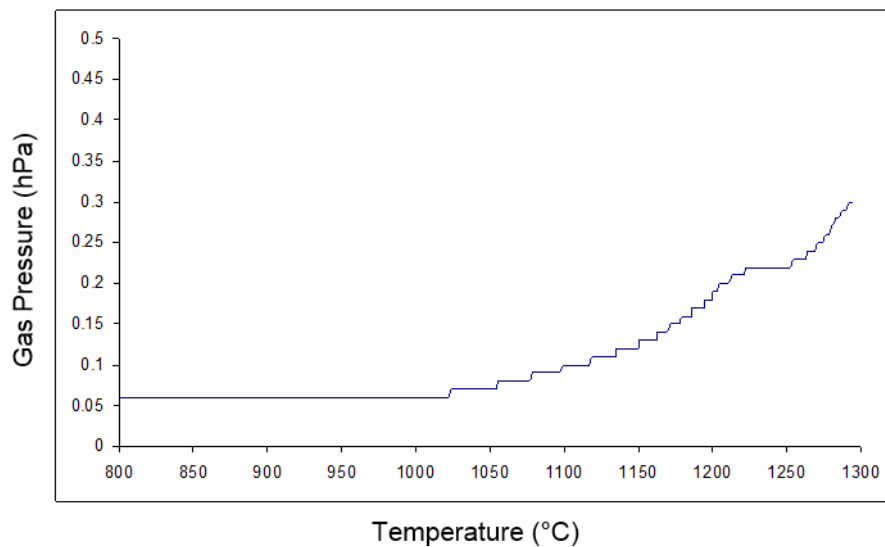


Figure 6.6: Outgassing from the SPS chamber. Recorded by Queen Mary University of London as part of the collaboration study by Watkinson et al. (2017b).

The objective of using a two-stage SPS process with commercially sourced CeO₂ was to allow the material to outgas and reduce at a lower temperature and pressure and then to allow the ceria to sinter at a higher temperature and pressure in order to mitigate the cracking observed in the specimens manufactured in a single stage. The fractured surfaces of the two-stage SPS discs A and B (made under conditions A and B shown in Figures 2a

and 2b, respectively), which were manufactured using commercial CeO_2 , are illustrated in Figure 6.7. Disc A was intact and disc B was broken on removal from the die. A small change in sintering profile from condition A to B resulted in a large change in relative density and microstructure: discs A and B had relative densities of 79 ± 1.2 % T.D. and 88 ± 1.4 % T.D., respectively, and disc B evidenced improved sintering when compared to disc A. Disc B also had small pores. The ground and polished fragments of disc A and disc B are shown in Figure 6.8. Disc A had a central lighter region and a darker border. It was not clear whether there was an evolution over time in the colour, and therefore in the oxygen to metal ratio, of this central region during the several months between when the disc was made, stored, and then ground and polished for analysis. To aid seeing this colour difference effect, the image contrast and brightness of the top left corner of the sample has been increased in Figure 6.8. The central region appeared porous as it readily absorbed the coloured polishing fluid. The mounted and polished disc B is also shown in Figure 6.8. It was much darker and did not show a colour gradient. Figure 6.8 also illustrates SEM images of the two polished discs. There was a clear difference in grain size and disc B evidenced grain pull-out.

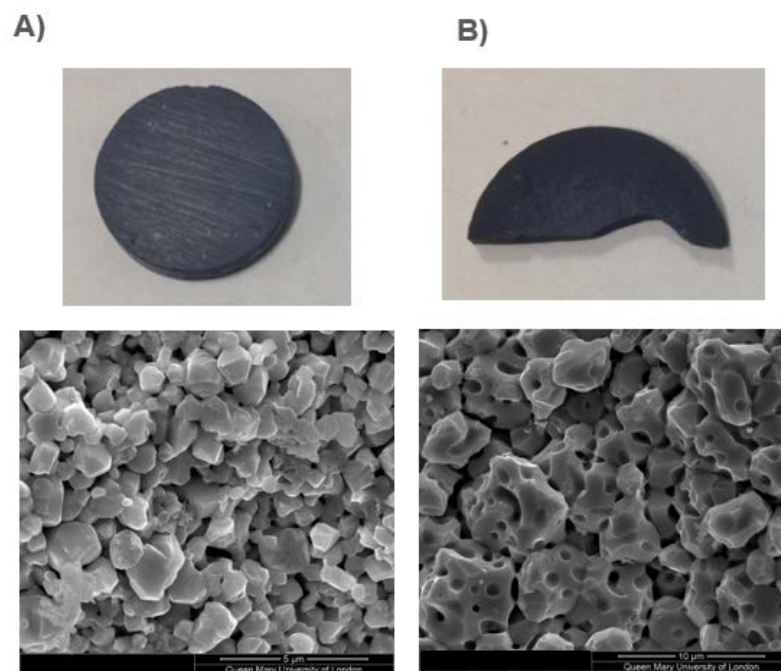


Figure 6.7: A) the fractured surfaces of disc A made by SPS Condition A (5 μm scale bar) and B) disc B made by SPS condition B (10 μm scale bar) using commercial CeO_2 .

Recorded by Queen Mary University of London as part of the collaboration study by Watkinson et al. (2017b).

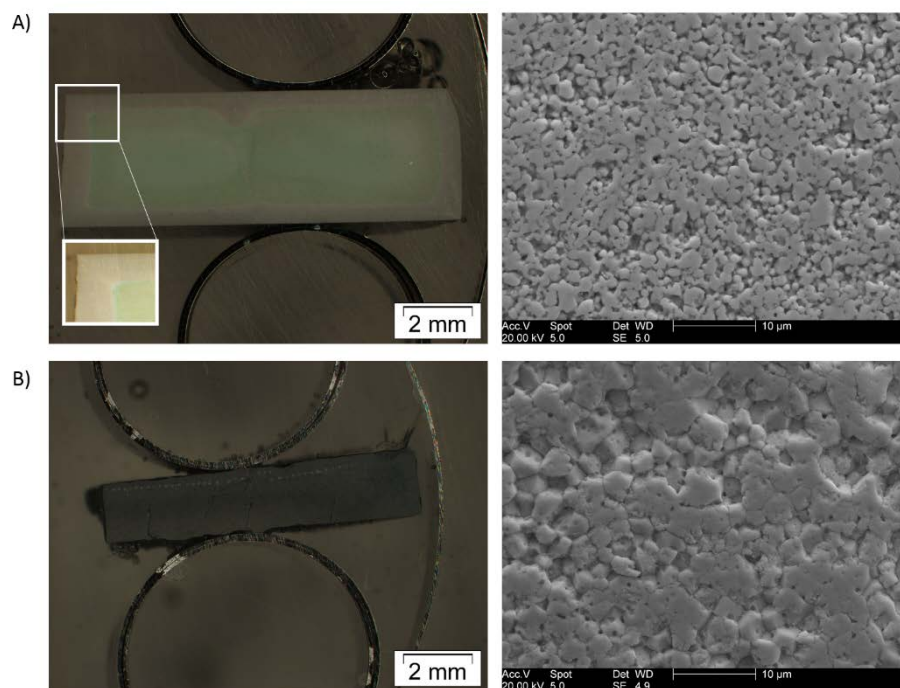


Figure 6.8: An optical image and SEM image of the microstructure of A) disc A and B) disc B, respectively. The top left corner of disc A is shown with an increased image contrast and brightness to aid the identification of the border region. The green and yellow colouration is an effect caused by absorption of the polishing fluid.

Relatively intact pellets were made by spark plasma sintering lath-shaped CeO_2 powders 1 and 2 (see Table 6.1) using sintering condition C (see Figure 6.2). These will be referred to as SPS pellets C1 and C2, respectively (C refers to sintering condition C and the numbers refer to the CeO_2 batch numbers). These structures had uneven surfaces particularly near the edges as shown in Figure 6.9. In addition, the edges showed signs of fragmentation. These were all observed on removal from the SPS die except for the large exposed area shown in pellet C2 that was produced by a spontaneous fracture a week after SPS. The pellets were dark grey immediately after sintering but gradually changed back to a beige colour. This is shown in the fragmented regions in Figure 6.9. This occurred despite efforts to store the samples in thermally sealed bags with the air expelled, which were packed in another bag with desiccant inside to minimise water absorption. The relative densities of pellets C1 and C2 were 85 ± 0.5 % T.D. and 84 ± 0.5 % T.D., respectively. Approximately 3.5 months after sintering, the pellets were removed from their vacuum packs. The samples fragmented and those associated with pellet C2 are shown in Figure 6.10. The fragments showed signs of colour change to beige. A significant portion of the SPS pellet C2 had turned beige with the central region still dark

grey as illustrated in Figure 6.10. The pellet could not be sectioned lengthways or in cross-section due to insufficient handling strength. A fragment of the original pellet was cold mounted in epoxy resin, ground and polished (see Figure 6.11). As the sample was ground, more of the beige material was removed and dark grey regions became more visible with some evidence of cracking.



Figure 6.9: Images of the pellets (a) C1 and (b) C2 (nominally Ø13 mm x 16 mm) 1 week after SPS.

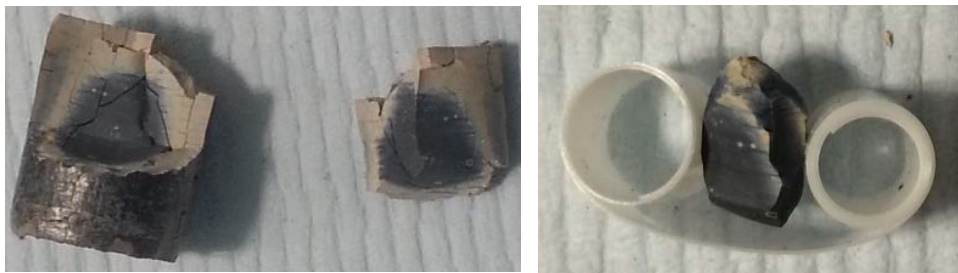


Figure 6.10: Two major fragments (left) of SPS pellet C2 approximately 3.5 months after manufacture, where the smaller fragment further broke up to leave smaller piece (right, shown at higher magnification).



Figure 6.11: The polished surface of SPS pellet C2.

3.1.2. Vickers Hardness of SPS CeO₂

For disc A, ten indents that were made using a Mitutoyo MVK-G1 Hardness Tester were analysed using SEM and all were acceptable on the basis of morphology alone (per ASTM C1327-08 (ASTM C1327 - 08, 2008)). Indent dimensions were measured twice per indent to account for operator variability, which resulted in two sets of hardness measurements for the sample. The mean Vickers hardness with its standard deviation is shown in Table 6.3. The mean hardness values were very similar for the two measurement sets (2.7 GPa *cf* 2.8 GPa), which are combined into a single mean in Table 6.3.

On disc B, indent morphology was affected by the extensive pull-out on the surface caused during grinding and polishing, as shown in Figure 6.8. This pull-out was consistent with Figure 6.7, which showed the grains in the fractured surface were not well consolidated. There is an element of subjectivity in assessing the acceptability of indents. In this case, they were judged not to be acceptable, and so no Vickers hardness values are reported for disc B in Table 6.3.

The near-net shaped pellet C2, which was manufactured using lath-shaped CeO₂, did not yield a sufficient number of acceptable indentations to allow a hardness value to be determined. The indentations had large amounts of grain displacement around them. The low resistance to indentation of this material was not unexpected given that the pellet had fragmented prior to cold mounting.

*Table 6.3: Comparison of Vickers hardness measurements. *Vickers hardness data were recorded by University of Dayton Research Institute as part of the collaboration study by Watkinson et al. (2017b).*

Material	Sintering Technique/ Profile	Disc	Vickers Hardness (GPa)	Standard Deviation (GPa)
CeO ₂	Spark Plasma Sintering/ Condition A; see Figure 6.2.	A	2.7	0.32
CeO ₂	Cold-Pressing-and- Sintering; see Figure 6.3.*	1	5.7	0.40
		2	5.5	0.26
		3	5.7	0.20
		5	6.4	0.25
Nd ₂ O ₃	1350 °C/50 MPa/3 min	20 mm disc	1.08	0.01

3.1.3. Cold-Press-and-Sinter Behaviour of Lath-shaped CeO₂

The powder particle properties of the input CeO₂ impacted the green disc handling strength to the extent that some powders could not be pressed successfully (batches 4 and 6 described in Table 6.1). Batches 1, 2, 3 and 5 were cold-pressed-and-sintered successfully and the dimensions and geometric densities are given in Table 6.4. The results show that the particle properties impact the sintered disc relative density. Discs 2 and 5 delaminated into three and two layers, respectively.

Table 6.4: Successful cold-press-and-sinter CeO₂ trials. Performed by University of Dayton Research Institute (UDRI) as part of the collaboration study by Watkinson et al. (2017b). The data are stated to a greater number of significant figures than in Table 6.2. This is because equipment with different sensitivities were used at the two institutions (UDRI and QMUL) to take the mass and spatial dimension measurements.

Batch #	Green Disc Thickness (mm)	Sintered Thickness (mm)	Sintered Diameter (mm)	Mass (g)	% Theoretical Density
1	2.21	2.10	6.78	0.4144	77 ± 10
2	2.01	1.90	6.99	0.4403	85 ± 12
3	1.80	1.70	7.39	0.4363	83 ± 12
5	1.83	1.80	7.01	0.3890	79 ± 12

3.1.4. Vickers Hardness of Lath-shaped CeO₂

The mounted and polished intact discs are shown in Figure 6.12. Vickers hardness tests were carried out using a Buehler 1600-6300 Vickers hardness tester in the numbered regions shown in Figure 6.12. SEM analysis was not required as the indents could be analysed optically with the indents in focus. The dark areas were regions infused with resin where specimen cracks were present. The average Vickers hardness values are outlined in Table 6.3.

The mean hardness values in Table 6.3 indicate that disc 5 was harder than disc 1, 2 and 3. The particle properties of the input material affected the Vickers hardness of the sintered body. Student's t-tests were conducted to separately compare the Vickers hardness data for discs 5 and 1, 5 and 2, and, finally, discs 5 and 3. Each of the three tests rejected the null hypothesis that mean Vickers hardness values of the two discs were the same to a confidence of greater than 95 %. Thus, the difference in the means are statistically significantly different in each case.

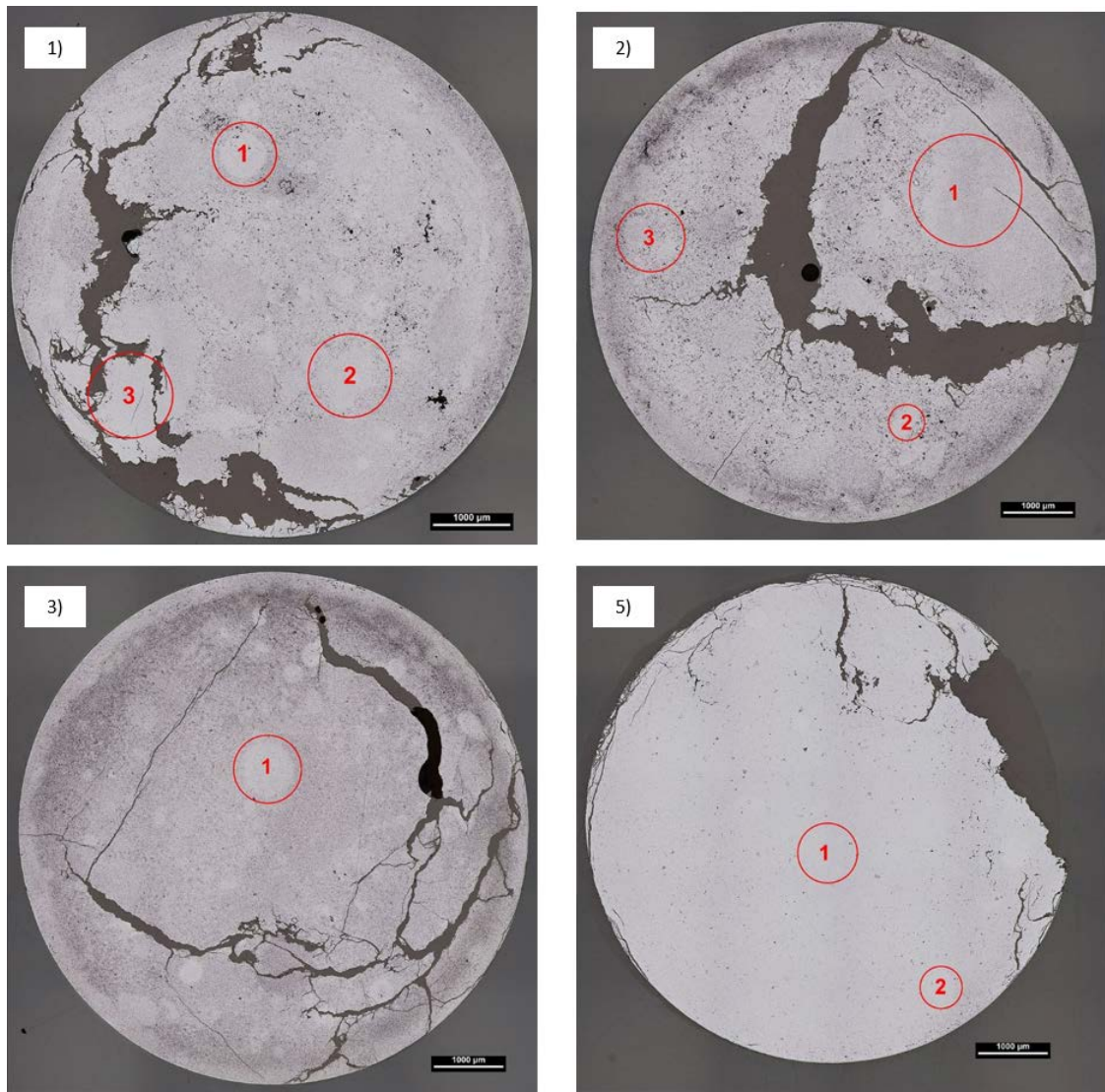


Figure 6.12: The polished surfaces of discs 1, 2, 3 and 5 cold-pressed-and-sintered discs (1 cm scale bars). Vickers hardness tests were conducted in the numbered regions. Performed by University of Dayton Research Institute as part of the collaboration study by Watkinson et al. (2017b).

3.2. Neodymium (III) Oxide

3.2.1. Demonstrating SPS of a Near-Net Shaped Pellet

Figure 6.13 illustrates the pellet sintered using commercial Nd_2O_3 and sintering profile C. It was intact and had a relative density of 98 % T.D. Figure 6.13 shows that like the CeO_2 pellets, the SPS of Nd_2O_3 did not result in perfect cylinders; they had material absent near the circular faces.

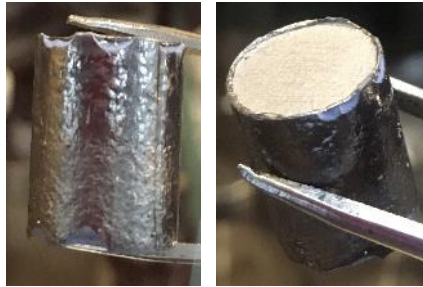


Figure 6.13: The SPS Nd_2O_3 pellet (nominally $\text{Ø}13 \text{ mm} \times 16 \text{ mm}$) sintered using Condition C (see Figure 6.2). Recorded by Queen Mary University of London as part of the collaboration study by Watkinson et al. (2017b).

3.2.2. Sintering to a Target Relative Density Range

Figure 6.14 illustrates the relative densities of the discs with 20 mm nominal diameter sintered at different temperatures. To achieve a target relative density of 85-90 % T.D., a near-net shaped pellet was sintered at 1080 °C. This pellet suffered some local edge fragmentation in a similar matter to the CeO_2 pellets manufactured by SPS as shown in Figure 6.9. The density of the resulting Nd_2O_3 pellet is also shown in Figure 6.14, and has a notably higher relative density (94 % T.D.) than predicted by the trend of the curve produced by sintering 20 mm diameters discs.

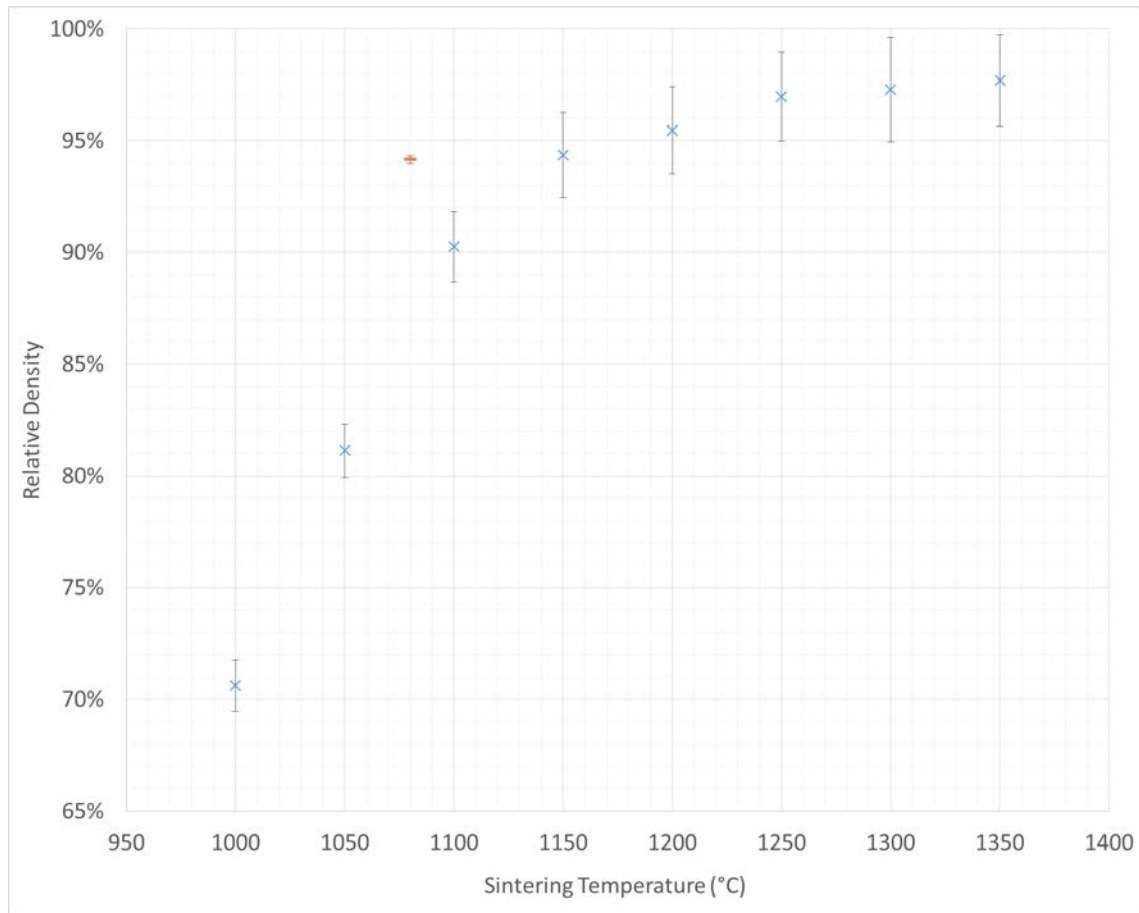


Figure 6.14: Illustrates the relative density versus sintering temperature results for the $\varnothing$ 20 mm Nd_2O_3 discs (blue crosses) and for the near-net shaped pellet (orange rectangle). Data recorded by Queen Mary University of London following discussion.

3.2.3. Vickers Hardness of Nd_2O_3

Vickers hardness tests were conducted on the 1350 °C disc from Figure 6.14. This disc was selected in an attempt to generate a bounding maximum Vickers hardness (it was sintered to the highest density) value for Nd_2O_3 and to maximise the chance of generating acceptable indents. Unlike with the spark plasma sintered CeO_2 , the acceptability of the Vickers indents could be made with the optical microscope of the hardness test machine. However, the acceptability of one indent was assessed using a higher resolution optical microscope. Ten out of eleven indents were deemed acceptable. The Vickers hardness is reported in Table 6.3, which shows that the value was notably lower than CeO_2 .

4. Discussion

4.1. CeO₂

4.1.1. *Spark Plasma Sintering Commercially Sourced and Lath-shaped CeO₂*

Spark plasma sintering with graphite is known to provide a reducing environment. Nearly all the spark plasma sintered CeO₂ discs or pellets were grey, which was consistent with the observations made by Bevan (1955) for CeO_{2-x}. Knachel et al. (2015) investigated the reduction behaviour of CeO₂ and produced samples with differing shades of grey or blue. They found that direct physical contact with graphite was not needed to cause the reduction. Thus, according to these pieces of literature, the grey appearance of the spark plasma sintered discs and pellets was indicative of the partial reduction of CeO₂. An example of sample outgassing during SPS was shown in Figure 6.6 for a disc fabricated using a one-stage process. The only sources for gas production would have been oxygen from the sample or the carbon monoxide or dioxide as a consequence of the reaction with the graphite die. It is likely that reduction of the CeO₂ as described by Zhou and Rahaman (1997) occurred during the experiment. Zhou and Rahaman (1997) attributed the observed weight loss in their CeO₂ powders to the reduction of the source material to Ce₂O₃. They state that the loss was particularly large beyond 1200 °C. The data presented in Figure 6.6 are in agreement.

Although an increase in temperature resulted in an increase in density for one-stage SPS, it was difficult to produce intact discs. A small change in SPS parameters resulted in a large change in disc density and in fracture surface microstructure. This was evidenced by both the one-stage and two-stage sintering trials. CeO₂ densification is thus difficult to control when using SPS. The 2-stage sintering profiles (condition A and B) were thought to have successfully produced intact 20 mm discs by permitting outgassing prior to densification. Although disc A was intact, the relative density was too low for the sintering conditions to be used further. The breakage in disc B whilst being removed from the die highlights that the handling strength of the material produced is still a concern.

On initial inspection, relatively intact pellets with relative densities in the mid-80 % T.D. were made using SPS when the particle properties of the input CeO₂ was changed from sub 5-µm agglomerates to larger lath-shaped particles, which were produced using the wet chemical process proposed for fuel manufacture. Both pellets C1 and C2 were not

perfectly cylindrical due to edge fragmentation. Thus SPS could not achieve the desired geometry and appears unlikely to be able to do so with reproducibility.

The colour change in the SPS pellets (sintered using synthesised lath-shaped CeO_2) to dark grey and back to beige suggested reduction and re-oxidation, respectively. The suspected changes in oxygen to metal ratio and the irregular edges of the compacts would have added some uncertainty to the density measurements. The fragmentation following storage suggested the handling strength had diminished significantly. It is likely this oxidation is a factor in the fragmentation observed. It is also possible that the differences in particle characteristics of the commercially procured and the wet-chemically synthesised (lath-shaped) materials had an impact on the oxidation; the discs made using the commercially sourced CeO_2 did not disintegrate into fragments. Given that AmO_2 has a greater tendency to reduce (Whiting et al., 2015), the complexity in spark plasma sintering AmO_2 is likely to be even greater.

4.1.2. Cold-Pressing-and-Sintering Lath-shaped CeO_2 with Varying Particle Sizes and Specific Surfaces Areas

Some of the cold-pressed-and-sintered ceria discs suffered from unwanted delamination. Americium oxide particles made via the oxalate precipitation and calcination route have similar lath morphologies; if the CeO_2 cold-press-and-sinter behaviour is indicative of AmO_2 , then methods into preventing delamination may need to be investigated.

The physical characteristics of the CeO_2 starting powder plays an important role in being able to press integral discs. Batch 3 pressed particularly well. However, the inability to press batch 4 and yet to be able to press batch 1 is unexpected as they had similar specific surface areas and particle size distributions (apart from d_{90} values) according to Table 6.1. The green strengths of the intact discs were not measured but their integrities were qualitatively assessed as adequate. Discs 2 had a relative densities that met the target of 85-90 % T.D., but disc 5 had a lower density (see Table 6.4). The Vickers hardness of disc 5 was greater than that of disc 2. Table 6.1 shows that the powder in batch 5 had a similar specific surface area to batch 2, but the estimated particle sizes were notably lower in batch 5. These data show no evidence of the nature of the relationship between particle size, specific surface area, sintering behaviour and hardness. They do indicate that changes to the production parameters of the powder have a significant impact on final

properties for this material. From this, it must be assumed that the situation will be similarly complex for americium oxide compounds.

4.1.3. Vickers Hardness Comparison of Spark Plasma Sintered and Cold-Pressed-and-Sintered CeO₂

Vickers hardness does not provide a direct indication of mechanical properties other than resistance to indentation. However, it provides an initial indication and means of comparison of the mechanical properties of these sintered CeO₂ discs and pellets. The processes necessary to prepare the specimen and generate valid hardness data do give an indication of potential practical issues with handling the material. Vickers hardness tests of the 2-stage spark plasma sintered discs A and B and pellet C2 indicated generally low resistance to indentation, with acceptable indents only achieved in disc A. The inability to obtain valid hardness data from an SPS pellet produced using lath-shaped CeO₂ particles indicates a potential concern for the use of this material (and AmO₂) and identifies an area for future work. Disc A had a much lower Vickers hardness than the cold-pressed-and-sintered discs (see Table 6.3). This again suggests inferior mechanical performance, perhaps attributable to the greater reduction during the sintering process disrupting the microstructure. A comparison of the measured Vickers hardness data in this study cannot be made with AmO₂ or Am₂O₃ due to the lack of published data. The mechanical properties of UO₂ are used as a reference for a nuclear material. The Vickers hardness of disc A was much lower than that of UO₂ (5.88 GPa) (Cardarelli, 2008), whereas the cold-pressed-and-sintered discs and pellets had hardness values that were consistent with UO₂. This indicated their resistance to indentation was comparable to a nuclear material.

In the context of future investigations, it is suggested that Vickers hardness tests should use reduced loads if cracking is prevalent i.e. lower than 300 gf; the ASTM standard suggests that if the majority of Vickers hardness indents in a given test produce cracks, then lower indentation loads should be used (ASTM C1327 - 08, 2008). However, should there be a desire to compare future data with the Vickers hardness data in this study, future tests will need to use the same load conditions (300 gf and 15 s dwell).

4.2. Spark Plasma Sintering Nd₂O₃

4.2.1. Initial Pellet Fabrication

It was demonstrated that a high relative density and intact Nd₂O₃ pellet can be produced by SPS. This was thought to be because Nd₂O₃ does not reduce as readily as CeO₂ as it is

already in a lower oxidation state (Arin et al., 2008). The sintering condition profile C (see § 2.2.3) resulted in a 98 % relative density. However, an Am_2O_3 pellet may not have the capacity to allow helium outgassing if Am_2O_3 were to behave like Nd_2O_3 under SPS i.e. to sinter to such a high density.

4.2.2. Demonstrating the Target Relative Density

Figure 6.14 illustrates that 20 mm diameter discs can be fabricated with relative densities of over 95 % T.D. at temperatures as low as 1200 °C. The disc sintered at 1350 °C had a comparable relative density to the pellet sintered using sintering profile C (Figure 6.2) despite the difference in aspect ratio and pressure. Although the near-net shaped pellet sintered at 1080 °C was expected to have a relative density within the target range (85-90 % T.D.) according to Figure 6.14, its relative density was much higher than expected at 94 ± 0.2 % T.D. The change in aspect ratio may have impacted the densification process. Future investigations need to be conducted to establish how target densities can be achieved for different ratios, particularly for a near-net shaped pellet geometry. More generally, the data present a clear drive for future studies of the sintering of these materials to use realistic aspect ratios in spite of the large volumes of material required.

The Vickers hardness value was much lower than the sintered CeO_2 (SPS and cold-pressed-and-sintered) discs for which acceptable data could be collected (see Table 6.3). Thus ceria can be spark plasma sintered or cold-pressed-and-sintered to have superior hardness to spark plasma sintered Nd_2O_3 . This is the first report of the hardness of Nd_2O_3 in the literature. Vickers hardness in ceramics is not a direct measurement of mechanical properties, and so the data only support the conclusion that there may be a concern about whether the handling integrity of Nd_2O_3 pellets is sufficient to make it an appropriate mechanical surrogate for americium oxide fuels.

5. Conclusions

Both the spark plasma sintering and cold-press-and-sinter techniques were able to sinter micrometric CeO_2 discs or pellets with relative densities within the target range of 85-90 % T.D. without ball-milling the surrogate fuel. Despite this, it has been shown that SPS is an unsuitable method to sinter CeO_2 due to the effects of reduction of the material. Intact high density discs could not be produced using commercial material and although relatively intact pellets could be made using larger lath-shaped particles (on initial

inspection), the pellets exhibited chipping (initial evidence of fragmentation) and eventual further fragmentation. The study suggests that SPS cannot enable pellets to be made with reproducible geometries without further development. Further to this, as the CeO_2 pellets eventually disintegrated into fragments, which indicated that the current method cannot make pellets with stable integrity. Although this may have been caused by gradual oxidation, and the effect of annealing pellets post-SPS could be explored, this will not address the non-reproducible geometry. The design of pellet containment layers in the RPS system will require the reduction extent, crystallographic phase changes and thermal expansion to be characterised. Future X-ray diffraction studies will be conducted to assess the CeO_2 reduction behaviour.

Although cold-press-and-sinter takes longer than SPS it has enabled intact CeO_2 discs to be made with near-target densities and with higher Vickers hardness. All cold-pressed-and-sintered discs had comparable Vickers hardness to current nuclear ceramics (represented by uranium dioxide, UO_2), whereas the only meaningful value for the SPS discs was much lower. However, discs manufactured from lath-shaped material by cold-press-and-sinter did exhibit delamination. Furthermore, the effects of differences in particle size and specific surface area of the raw material were found to be significant without it being possible to correlate these effects in this study. Future studies must therefore fully characterise the effects of differences in lath-shaped particle size and specific surface area with the aim of creating a reproducible and well-characterised surrogate fuel form. It is important to note that AmO_2 produced via an oxalate precipitation and calcination route has similar lath-shaped morphology and the same considerations may apply.

High-density intact Nd_2O_3 discs were successfully produced via SPS, along with the potential to tailor the density in the required range by adjusting the sintering parameters. Using a modified sintering profile for a near-net shape pellet yielded an average density of 94 ± 0.2 % T.D. with some surface fragmentation. This illustrates that the aspect ratio of the pellet affects the sintering parameters and behaviour. Future work on these materials must focus on representative geometries. Neodymium (III) oxide may be a suitable mechanical surrogate for Am_2O_3 ; however, the mean Vickers hardness, which was obtained from a limited data set, was much lower than for typical nuclear ceramics.

This work requires extension to consider the use of cold-press-and-sinter, and the effect of raw powder obtained from a wet chemical process.

Cerium and neodymium oxides represent potential mechanical surrogates for the americium oxide fuel under development for the ESA space radioisotope power systems. On the basis of the current studies, cold-press-and-sinter has fewer potential complications with reduction. Future research must consider the full effect of the wet-chemical processing parameters on particle characteristics and sintering behaviour in realistic pellet geometries.

6. Acknowledgements

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CHAPTER 7: RIETVELD REFINEMENT OF $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ POWDER X-RAY DIFFRACTION DATA

1. Introduction

Investigations into how to process and sinter americium oxide powders into pellets are being carried out as part of the ESA Programme's fuel development research. Fundamental to this, are the sintering trials with a variety of surrogates for a range of americium oxides. In Chapter 6, sintering investigations with CeO_2 and Nd_2O_3 were conducted to infer how AmO_2 and Am_2O_3 may sinter. The crystal structures of surrogates and the americium oxides may change during sintering. The changes that occur are likely to be affected by the sintering technique and profile used. It is essential that crystal structure phase changes and crystal lattice expansions are understood. Such changes may impact material consolidation during sintering. Such information may also impact the design of the americium oxide fuel containment systems.

As was discussed in Chapter 5, one of the americium oxides of interest to the ESA programme is a substoichiometric form, namely Ia-3 $\text{AmO}_{2-(x/2)}$. In that chapter, Ia-3 (C-type) $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ was proposed as a candidate surrogate. A synthesis method where Ce Nd oxalates were continuously co-precipitated from the reaction of oxalic acid and a mixture of Ce and Nd nitrates dissolved in nitric acid was used. The oxalates were then calcined to form $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$. An x-value of 0.60 was targeted by mixing the metal nitrates in an appropriate corresponding molar ratio. Qualitative powder X-ray diffraction (PXRD) analysis confirmed the synthesis of Ia-3 $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ material and quantitative X-ray fluorescence (QXRF) established that each material was made with a reproducible $\text{Nd}/[\text{Ce}+\text{Nd}]$ ratio of 0.62 with a coefficient of variation of around 0.1 % and an estimated uncertainty of ± 0.01 . It was thus confirmed that this co-precipitation method can be used to target an x-value for a Ce Nd based oxide solid solution.

The objective of the study described in this chapter was to determine the lattice parameter of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ material more precisely than was previously achieved in Chapter 5 via a simple peak position analysis method (Watkinson et al., 2017a). It was identified that Rietveld refinement analysis would be required. This refinement would:

1. Be useful for future sintering studies where crystallographic changes would need to be characterised particularly under different sintering conditions.

2. Allow a more precise inference of the x-value (using Equation 1 of Chapter 5) from XRD data to establish if it was consistent with the target value (0.6) and the QXRF determined value (0.62) of the previous study (Chapter 5), as well as the literature.

The scope of this work was to gain sufficient understanding of Rietveld refinement theory, and to gain sufficient training and knowledge in using MAUD (Material Analysis Using Diffraction) in order to be able to meet the objectives described above. MAUD is a piece of software developed by Lutterotti et al. (2004) that can be used to Rietveld refine X-ray diffraction data. Further details about the capabilities of MAUD as well as some basic tutorials in how to use can be found at the MAUD website (Lutterotti, 2017).

An introduction into the basic concepts and theory behind ‘Rietveld refinement’ is provided in § 2. More detailed descriptions of the theory are provided by Young (1993b) and Chateigner (2013a). The content outlined in § 2 is essential for understanding § 3 and § 4. The instrument needed to be calibrated or ‘defined’ (§ 3) before the X-ray diffraction data of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ could undergo Rietveld refinement (§ 4). The refinement of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ data is essentially presented as a standalone study. Consequently, the conclusion for refinement of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ powder X-ray diffraction data, and therefore of this chapter, is contained in § 4, namely, in § 4.5.

2. Background Theory and Concepts behind Rietveld Refinement

In this method of analysis, an XRD pattern is calculated using a number of models or functions and compared to an experimental pattern. The overall model is improved until the residual, which is described in greater detail in § 2.1, is sufficiently low. The functions that form the model describe different factors that contribute to describing an XRD pattern. Each function has its own variables or ‘parameters’ whose values are refined in order to improve the model. In fact, parameters are gradually introduced into the model and their values are refined.

There are several factors that contribute to describing the curve of an X-ray diffraction pattern. An introductory account of some of the key factors that influence a diffraction pattern is provided in the following sections. These sections include descriptions of some functions that can be used to model these influences. More extensive accounts of the various functions are described by Chateigner (2013a).

Some of the theory described is according to the introductory lecture provided by Dr L. Lutterotti (the developer of MAUD) at the annual MAUD school (Lutterotti, 2013). This is referenced accordingly.

2.1. The Intensity Equation and its Minimisation

An X-ray diffraction pattern comprises n data points. The parameters of the calculated pattern are allowed to vary so as to minimise the residual via a least-squared algorithm. In MAUD, a non-linear least-squared algorithm is used (Lutterotti, 2013). The residual, S_I , that is minimised over all n data points is

$$S_I = \sum_n w_n (I_n^{exp} - I_n^{calc})^2, \quad (1a)$$

where

$$w_n = \frac{1}{I_n^{exp}}, \quad (1b)$$

and I_n^{exp} and I_n^{calc} are the intensities of the n^{th} data point of the experimentally determined and calculated patterns, respectively (Lutterotti, 2013, Young, 1993a). Typically several iterations of the refinement are conducted before another parameter is introduced into the analysis to improve the model.

If it is assumed (for simplicity) that the sample being analysed comprises only one crystallographic phase, then the intensity of its modelled pattern (Lutterotti, 2013, Young, 1993a) is then

$$I_n^{calc} = s \sum_K^{No. Peaks} L_K |F_K|^2 \phi(2\theta_n - 2\theta_K) P_K A + b_n, \quad (2)$$

where

- s is the overall scale factor, which depends on the unit cell volume and the beam intensity. The beam intensity needs to be refined every time a new data set is analysed and is not a constant for the instrument. It is known as the scale factor in MAUD.

- L_K is the Lorentz-Polarisation factor, which depends on the instrument-geometry (Lutterotti, 2013). Further information can be found in more detailed texts (Chateigner, 2013a). Note K is a peak number that describes a given set of Miller indices (h, k, l).
- F_K is the structure factor, which is described in § 2.3.1.
- ϕ is the profile function, which describes the effects of the instrument and the sample on peak shape (see § 2.4).
- P_K is a function that describes the effect of texture (also known as preferred orientation) on the detected intensity (see § 2.3.2).
- A is the absorption factor, which describes the effect of sample absorption on beam intensity (Lutterotti, 2013).
- b_n is a function that describes the background intensity. A number of models can be used, such as a polynomial of degree Q , where Q is dictated by the analyst.

A cycle describes the set of iterations used to refine a given set of parameters.

2.2. Assessing the Fit

The progression of a refinement i.e. whether the model is improving, is assessed by inspecting R -factors (Young, 1993a), residual plots and parameters values between successive refinement cycles. For example, each parameter is examined to see if it is physically meaningful.

When conducting a refinement, the modelled pattern is often plotted on the same axes as the raw data pattern, which allows an initial visual inspection of the discrepancies. However, the accompanying residuals plot is much more informative and allows the analyst to address potential causes that could help improve the model. The reader is referred to the article by McCusker et al. (1999) for more details.

R -factors are frequently used to provide a “statistical comparison between the calculated model and the measured experiment” (Chateigner, 2013e, Jansen et al., 1994). There are many different R -factors (1993a). The R_{wp} is the ‘weighted pattern’ R -factor. It is defined as

$$R_{wp} = \left[\frac{\sum w_n (I_n^{exp} - I_n^{calc})^2}{\sum w_n (I_n^{exp})^2} \right]^{1/2}. \quad (3)$$

It is often a preferred R -factor for use as its numerator is the residual that is minimised during refinement (see Equation 1a, which together with 1b defines the variables of Equation 3). Another useful value is the ‘expected profile’ R -factor R_{exp} (Jansen et al., 1994). This is defined by

$$R_{exp} = \left[\frac{N - P + C}{\sum w_n (I_n^{exp})^2} \right]^{1/2}, \quad (4)$$

which is the minimum R_{wp} value obtainable for a given number of refined parameters (Lutterotti, 2013). The N , P and C refer to the number of data points, the number of refined parameters and the number of constraints in the refinement, respectively. Jansen et al. (1994) and Chateigner (2013e) provide detailed discussions of these R -factors and differences in their calculations that arise between different Rietveld refinement programs.

Finally, the goodness-of-fit (GoF) is the ratio (Lutterotti, 2013) of Equations 3 and 4 i.e.

$$GoF = \frac{R_{wp}}{R_{exp}}. \quad (5)$$

The factors that impact peak intensity, peak shape and peak position in an XRD pattern are described in § 2.3, § 2.4 and §2.5, respectively.

2.3. Factors that Affect Peak Intensity

2.3.1. Structure Factor Equation

The structure factor, F_K , for a given peak number K or F_{hkl} for longhand, is related to the scattering from each atom, j , within a unit cell. It is defined (Young, 1993a, Chateigner, 2013e) by

$$F_K = F_{hkl} = \sum_{j=1}^N O_j f_j e^{2\pi i(hX_j + hY_j + lZ_j)} t_j, \quad (6)$$

where h , k and l are the Miller indices and for each j^{th} atom within the unit cell (N atoms in total): O_j is its site occupancy, f_j is the atomic scattering factor, X_j , Y_j and Z_j describes its relative position in the unit cell, t_j is the temperature factor (Pecharsky and Zavalij, 2009). According to the International Union of Crystallography (2013), the structure factor describes the amplitude and phase of the diffracted wave from a given $h k l$ plane, where the former is related to the diffracted X-ray intensity.

X-rays are actually scattered from the electrons surrounding the atoms. Consequently, the value of the atomic scattering factor f_j depends on the electron density (Dove, 2002). In practice, f_j is fitted as a function $\sin(\theta)/\lambda$ for a range of ions and atoms and it is equal to the atomic number when $\sin(\theta)/\lambda$ equals zero. The atomic scattering factor decreases with increasing $\sin(\theta)/\lambda$ (Dove, 2002). Unlike neutron scattering, X-ray atomic scattering factors are similar for atoms with similar atomic numbers.

The temperature factor, t_j , is described using atomic displacement parameters e.g. B . According to Pecharsky and Zavalij (2009), the thermal motion of an atom is the key contributing factor to the combined effect of these parameters (for the case of X-ray diffraction). The reader is referred to Pecharsky and Zavalij (2009) for further details. Depending on the required precision of diffraction data Rietveld analysis, the temperature factor can be estimated to different extents. Firstly, an approximation assuming isotropic atomic displacements is described by

$$t_j = e^{-B_j \frac{\sin^2 \theta}{\lambda^2}}, \quad (7a)$$

where θ is the Bragg angle for the reflection, λ is the wavelength of the X-ray radiation and B_j is the isotropic atomic displacement parameter defined by

$$B_j = 8\pi^2 \langle u_j^2 \rangle. \quad (7b)$$

In Equation 7b $\langle u_j^2 \rangle$ is the mean-square of the isotropic displacement (Dove, 2002). In MAUD, the isotropic B_j for a given atom is termed B_{iso} . The advantage of neutron diffraction over X-ray diffraction is its ability to enable the precise determination of atomic displacement parameters (Hosokawa, 2012).

2.3.2. Texture (Preferred Orientation)

Texture describes how the crystallographic planes of a sample are not randomly oriented but instead have some preferred orientation. This causes the relative intensities of scattered X-rays from the crystallographic planes to differ from those of a sample that has its planes randomly orientated (the material is assumed to be the same otherwise), such that some planes scatter more and others less. Typically, sample preparation methods can be used in an attempt to mitigate such effects when the texture of a sample is not of interest e.g. by side-packing the powder in the sample holder (This is a standard powder preparation technique.). When such methods do not suffice, corrections can be made to the X-ray diffraction data to try and improve the fit of the modelled diffraction pattern. In this thesis, only the standard reference material that was used to calibrate the X-ray diffractometer exhibited notable texture i.e. this was not found for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ sample. Details of how this was considered can be found in § 3.

2.4. Factors that Affect Peak Position

2.4.1. 2θ Offset

The position of the peaks in a powder X-ray diffraction can be affected by a multitude of things. An offset in 2θ caused by the instrument's misalignment will result in an apparent shift in the peak positions when compared to standard reference materials (SRMs).

2.4.2. Sample Height Displacement

The powdered sample's holder is designed to ensure that the sample's surface is at the ideal height i.e. at the radius of the goniometer, provided that it is packed flat within the holder's recession and flush with the holder's sides. Incorrect powder sample packing can result in over-packing or under-packing of the sample, which results in the sample being displaced a distance h from its ideal position. This causes an apparent shift, $\Delta\theta$, in the 2θ positions of diffraction peaks in the recorded XRD pattern. However, this shift varies as

$\cos\theta$, which in turn causes an error in each 2θ value in a diffraction pattern (Fultz and Howe, 2013). The shift in the peak position of a PXRD pattern is thus not constant and varies across the pattern. In fact this causes a corresponding uncertainty in the d-spacing of a given diffraction plane, and hence the lattice. Further details are described by Fultz and Howe (2013).

2.4.3. Strain

Isotropic strain inside a material can act to change the lattice parameter, which, in turn, causes the positions of the peaks in a diffraction pattern to shift (Fultz and Howe, 2013). The shift is a function of angle ($\tan\theta$) and increases with an increase in angle up to θ equal to 90° (Fultz and Howe, 2013).

2.5. Factors that Affect Peak Shape

2.5.1. Strain and Crystallite Size

Each crystallite in a powder may exhibit differing degrees of strain, where some may be in compression and others in tension (Fultz and Howe, 2013). Consequently, there can be a distribution of strain-caused shifts (see § 2.4.3) in peak position for a given diffraction peak. There will then be corresponding distribution in lattice parameters. The result is peak broadening. If the strain is hkl direction dependent, then it is known as anisotropic.

An ideal powder comprises a very large number of randomly oriented crystallites that have sizes under $10\text{ }\mu\text{m}$ (Zhan et al., 2007). The width of the diffraction peaks will be influenced by the size distribution of the crystallites that comprise the sample. Peak broadening increases with a decrease in crystallite size (He, 2013). The sizes of crystallites in the tens to hundreds of nanometres can be characterised (Ohara et al., 2008).

If the size of a crystallite is independent of the Miller indices i.e. h , k and l , such that it grows equally in all directions, then the crystallite size is referred to as isotropic (Leoni, 2014). However, if there is a variation in crystallite growth for different planes then there is anisotropy i.e. the crystallites are not spherical (Balzar and Popa, 2004). Popa (1998) found that this variation is dependent on the Laue group (see Glossary), and the strain distribution is also Laue group dependent. The effect of anisotropic crystallite size and strain can be modelled in MAUD using the *Popa* model. Popa (1998) outlined the separate mathematical series that describe the anisotropic crystallite size and strain for each Laue group. Each series can be simplified to an isotropic case. In the case of the crystallite size

series expansion, this corresponds to single term expansion e.g. anisotropic crystallite size₀, which is stated in the results of § 4.3. The reader is referred to the article by Popa (1998) for more details.

2.5.2. Instrumental Broadening

The observed profile or curve of the diffraction pattern is the convolution of an instrument contribution, $g(x)$, and the sample contribution, $f(x)$, with the background contribution added

$$\begin{aligned} h(x) &= [f(x) * g(x)] + b(x) \\ &= \int_{-\infty}^{\infty} f(x')g(x - x')dx' + b(x), \end{aligned} \quad (8)$$

where x is the difference between the measured 2θ position of a peak and its calculated position according to its Miller indices, x' is a ‘dummy’ variable used for the integration and $b(x)$ is the background (1993a, Chateigner, 2013e).

The instrument contribution to a recorded profile depends on the *geometrical configuration* of the diffractometer and its components (Chateigner, 2013e). It also depends on the *characteristics* of the emitted radiation, such as the spectral distribution (Chateigner, 2013e). The reader is referred to the paper by Lutterotti and Scardi (1990), which summarises the key relations involved. The following paragraphs outline the parameters that need to be refined to define the instrument contribution to a diffraction pattern. These refined parameters of the instrument ‘definition’/calibration are outlined in § 3.3.

Firstly, peak asymmetry is considered. The peaks in a diffraction pattern will have some asymmetry that varies with 2θ (Lutterotti and Scardi, 1990, Chateigner, 2013e). For the purpose of identifying the parameters that are refined in MAUD, the equation for the model is (Lutterotti and Scardi, 1990)

$$A(2\theta) = e^{-a_s|\theta - \theta_{K\alpha 1}| \tan \theta_{K\alpha 1}}, \quad (9)$$

where a_s is the refinable asymmetry parameter. In MAUD this is actually can be expressed as a series of terms that are refined, namely, *asymm0*, *asymm1* etc. where the latter is a small linear deviation from *asymm0*. The $\theta_{K\alpha 1}$ is the Bragg angle of a Cu $K_{\alpha 1}$ peak.

The following function that is often used to describe the full-width-at-half-maximum, H , is attributed to Caglioti et al. (1958),

$$H^2 = U \tan^2 \theta + V \tan \theta + W, \quad (10)$$

where U , V and W are parameters that are refined. Although this equation was originally developed to analyse neutron diffraction data it is widely used in commercial software to analyse X-ray diffraction data e.g. MAUD.

Finally, it is noted that the line broadening is typically described by a pseudo-Voigt function (Chateigner, 2013e), which is modelled in MAUD as

$$PV(2\theta) = (1 - \eta)L(2\theta) + \eta G(2\theta), \quad (11)$$

where L and G are Lorentzian and Gaussian functions, respectively, and η is a value between zero and one. It is this value that is refined. In MAUD, it can be expanded as a series where the parameters are denoted as Gaussian0, Gaussian1 etc. The latter refers to a small linear deviation from η .

3. Instrument ‘Definition’/Calibration

In § 2, a broad introduction into the various factors that influence the shape of an X-ray diffraction pattern was provided. It was established that the broadened profile of a peak is the result of the convolution of an instrument (diffractometer) contribution and a sample contribution (see § 2.5.2).

Before the X-ray diffraction data of the sample of interest can be analysed using Rietveld refinement, the instrument needs to be ‘defined’ (the term often referred to when using MAUD) in order to account for its contribution to sample data. This requires refining the XRD data of a ‘standard reference material’ (SRM) (Chateigner, 2013d). The objective is to use an SRM with sufficiently large crystallite sizes and minimal microstrain such that the line broadening due to the sample is minimised (Chateigner, 2013b). Ideally, the SRM certificate will state the crystallite size and microstrain. The SRM will have its crystal structure and properties such as crystallite sizes well defined. The result of the Rietveld refinement is that the instrument line broadening contribution to the XRD pattern is determined i.e. the U , V and W parameters of the Caglioti equation (Equation 10), the asymmetry parameters and the Gaussian fraction, which were all described in § 2.5.2.

The instrument response is then stored in the MAUD software. A Rietveld refinement of the XRD data of the sample of interest can then be conducted, which accounts for instrumentation contribution.

3.1. The National Institute of Standards & Technology (NIST) SRM 1976b Al₂O₃ (Corundum) Structure

The NIST lanthanum hexaboride, LaB₆ standard reference material, namely SRM 660c, is often used to determine the instrument contribution of a diffractometer. It can be used for calibrating line positions and shapes using powder diffraction (NIST, 2015b). It comprises isotropic crystallites that enable a powder to be prepared without texture (Chateigner, 2013d) and has zero microstrain. However, owing to constraints, the only SRM available was the 1976b Al₂O₃ in its corundum structural form (trigonal). Although it is less favourable as its primary use is for the calibration of diffraction line positions and not line shapes, the NIST certificate states that the SRM exhibits minimal microstrain and thus resultant line broadening, but that it “is detectable as a Gaussian broadening with a $\tan\theta$ dependence” (NIST, 2015a). It then proceeds to say that as there is an “essential absence of crystallite size broadening, SRM 1976b can be used to obtain an approximation of the instrument profile function (IPF)” (NIST, 2015a). The 1976b corundum sample was thus used in this analysis.

The SRM is a sintered compact comprising platelet particles. The sample was known to have some texture resulting from the pressing of the platelets to make the compact. The certified lattice parameters of the sample are outlined in Table 7.1.

Table 7.1: The NIST Certified Lattice Parameters for SRM 1976b (NIST, 2015a).

Lattice Parameter	Value (Å)
a	4.759137
c	12.99337

3.2. Data Acquisition and Observations

As per the PXRD analysis conducted in Chapter 5, a Bruker D8 Advance Powder Diffractometer equipped with a LynxEye Position Sensitive Detector in a flat plate (Bragg-Brentano) θ - θ configuration was used to acquire the data for the corundum and Ce Nd oxide samples. The source was CuK α radiation (a Ni-K β was used). The 2θ angular range from 4° to 90° was analysed using a 0.01° 2θ step size and a 0.5 second count time per step.

On inspection of the raw data it was evident that several of diffraction peaks displayed features neighbouring each Cu K $\alpha_{1,2}$ doublet. Examples of this are shown in Figure 7.1. The corundum material was certified to contain no crystallographic impurities (NIST, 2015a); therefore this was rejected as a possible cause. An investigation (See Appendix D) was conducted, which had two objectives: (1) to try to identify the cause for such an effect, and (2) to assess whether the effect could be modelled using Rietveld refinement analysis.

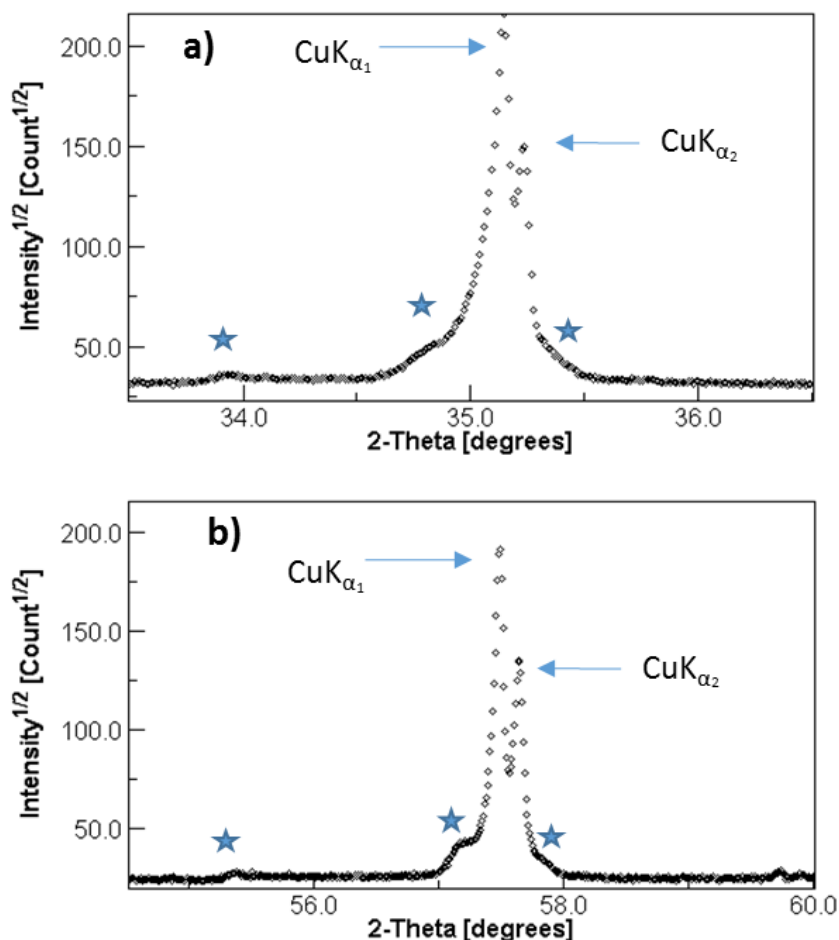


Figure 7.1: Examples of two corundum diffraction peaks, namely a) the (110) reflection and the b) the (116) reflection. The Cu $K\alpha_{1,2}$ doublets are labelled. Neighbouring ‘features’ were identified, which are labelled with stars.

3.3. Rietveld Refinement

MAUD (version 2.65) was used to conduct the Rietveld refinement. The Crystallographic Open Database (COD) file 1000032 for corundum (Al_2O_3) by Lutterotti and Scardi (1990) was adapted as the phase file for the analysis. Its lattice parameters were changed to conform to that of the SRM (see § 2.1). The wavelengths of the Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation were assumed to be 1.5406 Å and 1.54439 Å (in accordance with the Bruker D8 data) where the intensity of the former was twice that of the latter.

The background was modelled as a 5th degree polynomial. Parameters were then refined in the following order: background and intensity scale; the asymmetric0 and 1 term, Caglioti U , V , W terms, and Gaussian0 and Gaussian1 terms. As the SRM certificate suggested that the corundum comprised isotropic crystallites with an “essential absence of crystallite size broadening” (NIST, 2015a), a large crystallite size was imposed in the analysis to reflect this. A value of 2 μm was nominally chosen.

As will be seen in § 3, the Rietveld refinement of the Ce Nd oxide was successful and did not require texture to be modelled. However, as was stated in § 3.1, the corundum SRM did exhibit texture, which needed to be modelled in order to complete the calibration of the instrument. It was beyond the time scope of this project to gain expertise in texture analysis. In collaboration with Prof. D. Chateigner (see Acknowledgements), the refinement of the corundum SRM was completed. The texture models in MAUD were used to complete the calibration.

A number of different texture models were considered: ‘standard functions’, spherical harmonics and arbitrary texture. Explanation of these models can be found in the following references by Lutterotti et al. (2007) (for the first), Chateigner (2013c) and Fong (2013) (for the latter two). The standard functions fibre model was used to assess if the texture could be described using a single texture component. A fibre texture describes the scenario where crystallites align one of their crystal directions along one of the sample directions, as shown in Figure 7.2. Although the resulting R_{wp} was 10.1 % (to 3 s.f.), the spherical harmonics model was then implemented to see if an improvement would result. An R_{wp} of 9.98 % was achieved.



Figure 7.2: Diagram to illustrate the random orientation of crystallites about the fiber axis in a crystalline fiber.²⁹

An arbitrary texture model provided an unacceptable fit as did further refinement on removal of the model. In the penultimate refinement, the spherical harmonic texture model was applied once again with a cylindrical. Sample height displacement was also refined. The isotropic atomic displacement factor (B_{iso}) was fixed to 0.44 for the Al and O atoms. An R_{wp} value of 8.90 % was achieved. In the final analysis step, an arbitrary structure model was implemented with the aim of improving the fit further. The fit had a similar R_{wp} value (8.95 %).

²⁹ Image reuse from Neutron Scattering in Biology, High-Angle Neutron Fiber Diffraction in the Study of Biological Systems, 2006, p. 86, V. T. Forsyth and I. M. Parrot, © Springer-Verlag Berlin Heidelberg 2006 [see end of chapter for the full original copyright notice as required by the terms and conditions for reuse of this image]) With permission of Springer. Note the caption is required to be restated in according to the original source (Forsyth et al., 2006). It used the American spelling for fibre in the caption.

The final refined pattern is shown in Figure 7.3 and the refined parameters stored for the instrument are outlined in Table 7.2. With the calibration completed, the Ce Nd oxide was then analysed to address the research objectives of this chapter.

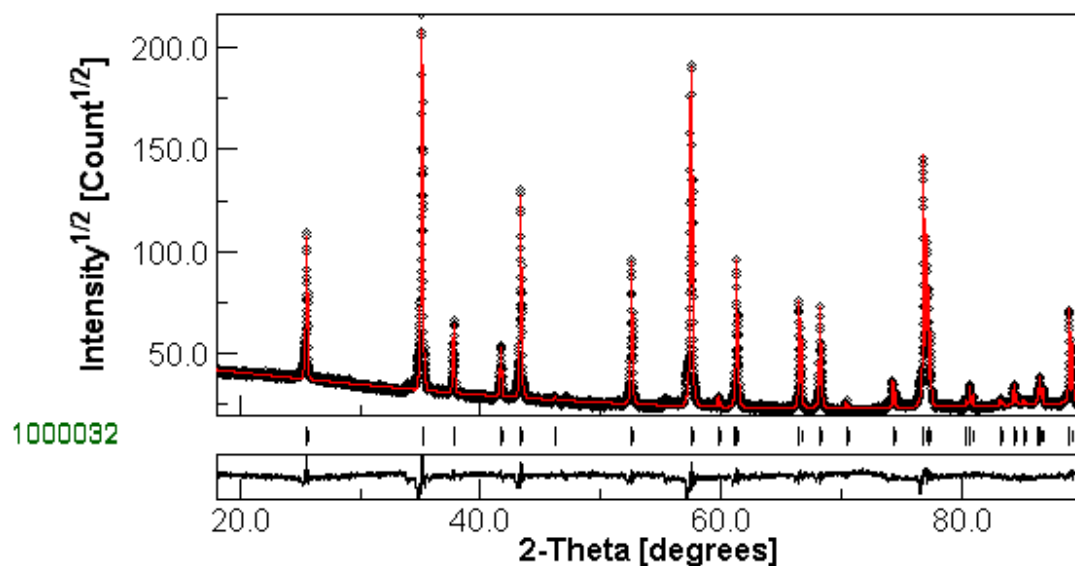


Figure 7.3: Illustrates the experimental PXRD pattern for SRM corundum (black diamonds) and the Rietveld refined pattern in (red line). The residuals of the fit are also shown. COD file 1000032 by Lutterotti and Scardi (1990) was adapted as the phase file.

Table 7.2: The Refined Instrument Parameters of the Bruker D8 Advance.

Parameter	Value
Asymmetry Value0	68.9(4)
Asymmetry Value1	-0.19(1)
Caglioti, U	$6(1) \times 10^{-4}$
Caglioti, V	$-1.3(5) \times 10^{-3}$
Caglioti, W	$4(5) \times 10^{-3}$
Gaussian, Value0	1.02
Gaussian, Value1	Fixed to 0

4. Rietveld Refinement of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ Powder X-ray Diffraction Data

4.1. Introduction

The volume of the unit cell of a solid solution phase is related by some function to its molar composition (fraction) e.g. x . In the case of cubic systems, this thus corresponds to a relationship between the unit cell parameter and the x -value. Assuming the relationship is known for a given solid solution system, then the molar composition of a given phase can be inferred by using an experimentally determined lattice parameter. In the case of $\text{AmO}_{2-(x/2)}$ species and their surrogates, this means that an estimate of the oxygen-to-metal ratio can be determined. It therefore should provide an alternative method to thermogravimetric analysis, and in the case for Ce Nd mixed oxide surrogates, to QXRF.

In Chapter 5, the relationship developed by Horlait et al. (2011) was introduced. It did not follow Vegard's law (Tilley, 2004), but was in fact a quadratic equation that describes the variation of the lattice parameter with x for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system up to x equal to 0.73. For the readers' convenience this relationship is restated,

$$a = -5.366 (R_{i\text{Ce}}(1-x) + R_{i\text{Nd}}x)^2 + 12.10 (R_{i\text{Ce}}(1-x) + R_{i\text{Nd}}x) - 1.281 \quad (12)$$

The $R_{i\text{Ce}}$ and $R_{i\text{Nd}}$ terms referred to the Ce and Nd ionic radii, respectively, and were assumed to be equal to 0.97 Å and 1.109 Å, respectively (Horlait et al., 2011). The transition of the solid solution from an F-type cubic phase (Fm-3m) to the superstructure C-type cubic (Ia-3) phase (see Chapter 5 for more details) requires the C-type phase to have a lattice parameter that is twice as large as the F-type phase. However, as the x-value proceeds to increase, the lattice parameter continues to expand. In order to compare the lattice parameter variation of the system with an increase in x, Horlait et al. (2011) halved all lattice parameters for the C-type (Ia-3) phases.

In Chapter 5, an initial estimate of the lattice parameter of synthesised C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a 0.62 Nd/[Ce+Nd] ratio was determined to be 5.51 Å +/- 0.01 Å. This was calculated from the 2θ positions of specific diffraction peaks, which were determined by fitting Gaussian profiles to them. Additionally, Equation 12 was used to predict the half-value lattice parameter that would be expected for a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ phase with an x-value of 0.62. This was confirmed to be 5.51 Å to 3 s.f. The results were thus consistent.

The Rietveld refinement investigation is described in the following sections.

4.2. Method

A cerium neodymium oxide was synthesised using the method outlined in Chapter 5. It was thus assumed to have an Nd/[Ce+ Nd] ratio, and thus an inferred x-value, of 0.62(1). An agate pestle and mortar was used to process the Ce Nd oxide material into a powder. The previous scanning electron microscopy analysis found the oxalate material was composed of lath-shaped particles (see Chapter 5). The literature suggested that the morphology is conserved on calcination to the oxide (Horlait et al., 2011). It was suspected that this morphology could cause preferred orientation effects (texture) in the powder X-ray diffraction data. The material was thus side-packed in order to reduce the impact.

A Bruker D8 Advance Powder Diffractometer (with a LynxEye Position Sensitive Detector) was used to acquire the diffraction data using Copper Kα radiation in a Bragg-Brentano θ-θ configuration. A Ni Kβ-filter was used. Data were acquired between 18 to

90° 2 θ using a step size and counting time per step of 0.01° 2 θ and 5.0 seconds, respectively.

Following the ‘definition’ of the instrument that was described in § 3, the MAUD (Materials Analysis Using Diffraction) programme was used to Rietveld refine the Ce_{1-x}Nd_xO_{2-(x/2)} acquired diffraction data (Lutterotti et al., 2004). The ICDS 155394 file for Ia-3 Ce_{0.5}Nd_{0.5}O_{1.75} by Chakraborty et al. (2006) was adapted as the phase file. Although their diffraction data were recorded using a neutron source, it provided an initial starting point for the analysis by providing nominal values for the lattice parameter, occupancy, fractional atomic positions (X, Y, Z) and isotropic atomic displacement parameters (B_{iso}) of the analysis.

The zeroth order background term and overall scale factor were initially visually estimated. The background was modelled using a 4th degree polynomial. The analysis proceeded with the refinement of the intensity scale and unit cell parameter, followed by the 2 θ offset and then the sample height displacement. The isotropic crystallite size parameter was refined and a default microstrain value of 6×10^{-4} was assumed. In an attempt to establish the impact of an anisotropic size distribution on the refinement, the Popa model (Popa, 1998) was employed where the zeroth (isotropic) and then the first order parameters were refined. As Ce and Nd ions have similar atomic numbers, it was unlikely that the X-ray diffraction data would be able to refine the occupancies of the Nd and Ce ions. Consequently, a measured Nd/[Ce+Nd] ratio of 0.62 was assumed (see Table 7.3). The refined structural parameters of Ce_{0.5}Nd_{0.5}O_{1.75} by Chakraborty et al. (2006) were consulted to identify the fractional atomic positions that were permitted to vary in Ia-3 (C-type) Ce_{1-x}Nd_xO_{2-(x/2)}. For convenience, their structural data are stated in the top half of Table 7.3. As X-rays are less sensitive in the determination of B_{iso} parameters than neutrons, the B_{iso} values of all atoms were assumed to be the same as Chakraborty et al. (2006) who refined neutron diffraction data. The occupancies for the oxygen atoms were then refined, followed by the zeroth order microstrain term for the Popa (1998) model and the B_{iso} value for the O1 (that for O2 was equated to it).

4.3. Results

The recorded PXRD pattern and the refined pattern are shown in Figure 7.4. The refined structural parameters and other parameters such lattice parameter are outlined in Table 7.3 and Table 7.4, respectively. The half-value of the lattice parameter was thus 5.51070(8) Å. The relationship between the lattice parameter and the x-value for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system (for x-values up to 0.73), namely, Equation 12, is shown in Figure 7.5. The experimental data of Horlait et al. (2011) is also illustrated. The half-value of the lattice parameter refined in this study is plotted in Figures 7.5a and 7.5b where the x-value was assumed to be that of the QXRF analysis 0.62(1), for the purpose of plotting.

To provide a more precise estimate of the x-value according to the half-value refined lattice parameter, the quadratic Equation 12 was solved for x. The solution was an x-value of 0.60 (even when the uncertainty in a was considered).

As stated previously, Equation 12 was used in Chapter 5 (it was Equation 1) to predict the half-lattice parameter of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with an $\text{Nd}/[\text{Ce}+\text{Nd}]$ i.e. x-value of 0.62 (from the QXRF analysis). The result was 5.51 Å to 3 s.f. As the Rietveld refinement has been able to determine the value more precisely, the predicted lattice parameter, together with its uncertainty associated with the QXRF analysis are stated for a comparison: Equation 12 predicts that $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with an x-value of 0.62(1) will have a lattice parameter of 5.513(1) Å to 4 s.f.

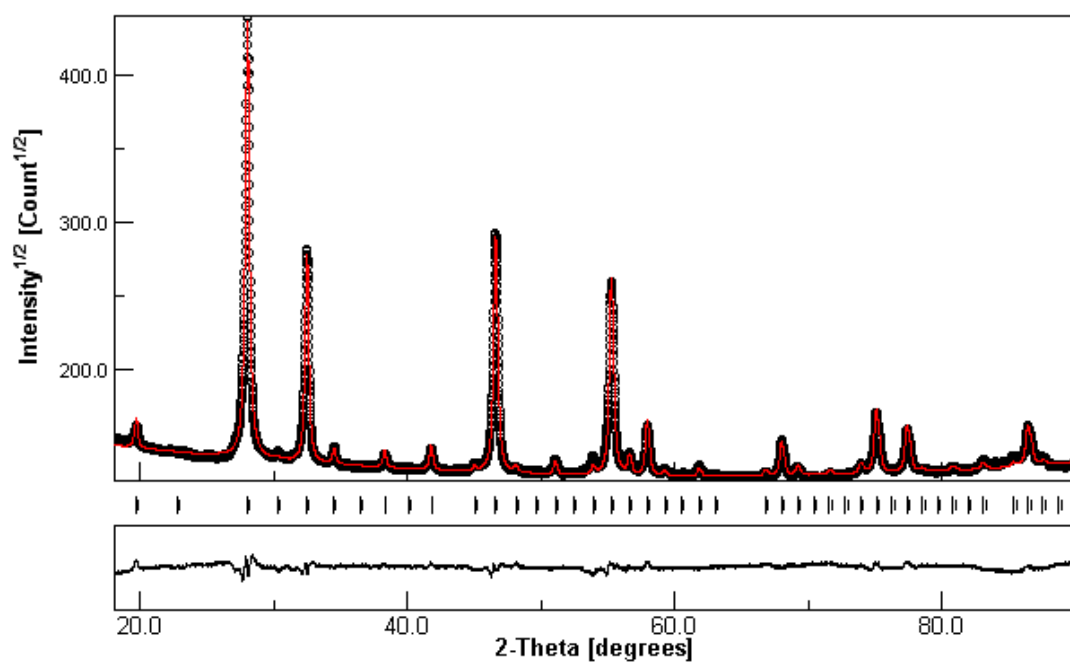


Figure 7.4: Illustrates the experimental PXRD pattern for the synthesised Ia-3 $Ce_{1-x}Nd_xO_{2-(x/2)}$ (black circles); the Rietveld refined pattern (red line) and the residuals of the fit. ICDS 155395 by Chakraborty et al. (2006) was adapted as the phase file.

*Table 7.3: The refined structural atomic parameters of Chakraborty et al. (2006) are stated in the top half of the table and the structural parameters of this study are provided in the bottom half of the table. * Fixed according to QXRF assumption from the Chapter 5.*

Atom	Site	X	Y	Z	B_{iso} (Å ²)	Occupancy
<i>Chakraborty et al. (2006)</i>						
Nd1	8b	0.250	0.250	0.250	1.293(118)	0.0833
Ce1	8b	0.250	0.250	0.250	1.293(118)	0.0833
Nd2	24d	-0.01306(35)	0	0.250	0.893(39)	0.25
Ce2	24d	-0.01306(35)	0	0.250	0.893(39)	0.25
O1	48e	0.38261(45)	0.13676(48)	0.37949(64)	1.305(42)	0.918(6)
O2	16c	0.38447(78)	0.38447(78)	0.38447(78)	2.431(181)	0.252(5)
<i>This study</i>						
Nd1	8b	0.250	0.250	0.250	1.293	0.62*
Ce1	8b	0.250	0.250	0.250	1.293	0.38
Nd2	24d	-0.0174(1)	0	0.250	0.893	0.62
Ce2	24d	-0.0174(1)	0	0.250	0.893	0.38
O1	48e	0.386(1)	0.145(2)	0.372(2)	1.305	0.885(8)
O2	16c	0.447(1)	0.447(1)	0.447(1)	2.431	0.31(3)

Table 7.4: *Refined for the Nd2, O1 and O2 atoms, and that for the Ce2 atom was set equal to that for Nd2 to minimise the number of refinable parameters.

Parameter	Value
Lattice Parameter, a (Å)	11.0214(2)
Sample Height Displacement (µm)	118
2θ offset	0.0080(6)*
Popa Rules: Anisotropic crystallite size0; 1	385.3(8)*; 0.068(5)*
Popa Rules: Anisotropic microstrain size0	4.0(2) x 10 ⁻⁴ *
R _{wp} (%)	2.45
R _{exp} (%)	0.708
Goodness of Fit	3.45

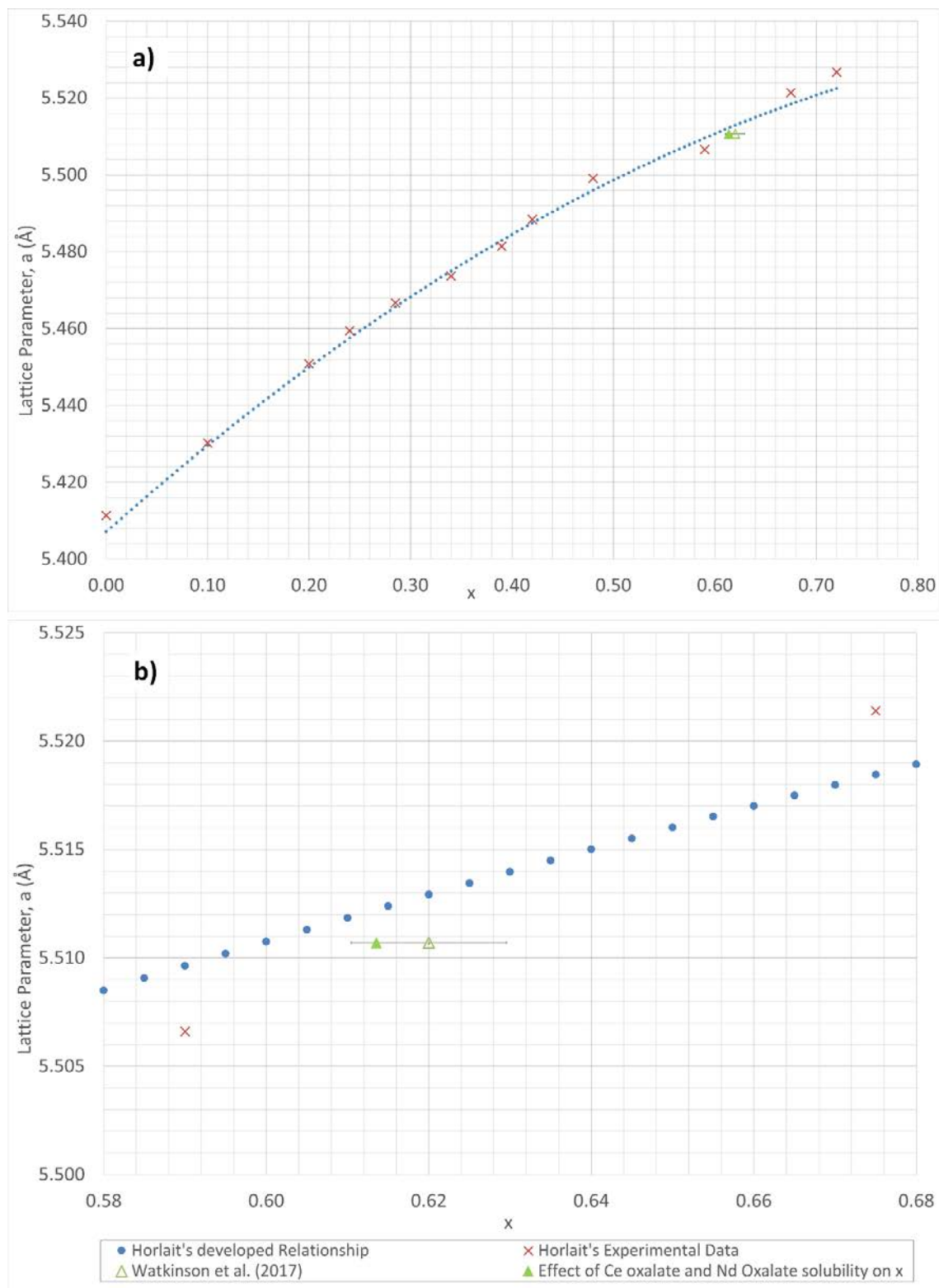


Figure 7.5: Illustrates the lattice parameter- x relationship developed by Horlait et al. (2011) for the $Ce_{1-x}Nd_xO_{2-(x/2)}$ system a) over the entire x -range that the relationship's valid for and b) over x -values near 0.62. See the Figure for key.

4.4. Discussion

In Chapter 5, it was observed that the oxalate particles were lath-shaped in morphology. This was also expected for the oxides. Therefore, it was expected that the particles may have a preferred orientation when packing even if they were side packed. However, the data were refined well without the need for texture analysis. This result was unexpected. The refinement results in Table 7.4 suggest the crystallites within the particles were near-isotropic and spherical.

In this study a Ce Nd oxide made using the process described in Chapter 5 has undergone PXRD analysis and its lattice parameter has been refined to be 11.0214(2) Å. The R_{wp} and Goodness of Fit parameters (see Table 7.4) together with the residuals (see Figure 7.4) indicate that a good fit was achieved.

Figures 7.5a and 7.5b show that the lattice parameter of the oxide is consistent with a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ solid solution with an x-value of ~ 0.6 . The solution of the quadratic Equation 12 confirmed this. The uncertainty in Equation 12, and therefore in the uncertainty in the solution, cannot be commented on quantitatively. However, it is not unreasonable to make this qualitative assessment of consistency, particularly if one considers the deviation in the experimental data of Horlait et al. (2011) from the plotted Equation 12 in Figure 7.5b as indications of the uncertainty e.g. for x equal to 0.59 and 0.675.

The x-value result of this study is consistent with the assumed quantitative XRF value of 0.62. An objective of Chapter 5 was to target the fabrication of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with x-values of 0.6 by mixing the Ce and Nd nitrates inputs of the oxalate precipitation process in this ratio. It was previously noted that the differences in Ce and Nd oxalate solubility could have impacted the expected ratio (see Chapter 5). An estimate of the expected ratio is shown in Figures 7.5a and 7.5b. This Rietveld refinement study to determine the lattice parameter of such an oxide confirms that an x-value of ~ 0.6 has been achieved and is thus consistent with the target x-value and the expectation.

4.5. Conclusion

The lattice parameter of synthesised Ia-3 $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with an assumed $\text{Nd}/[\text{Ce}+\text{Nd}]$ ratio of 0.62 was determined by Rietveld refinement. Rietveld refinement of the X-ray diffraction pattern has enabled a more precise estimate of the lattice parameter to be determined than was previously achieved using Gaussian peak fitting (see Chapter 5). The study corroborates with QXRF inferred x-value of 0.62 and the targeted x-value of 0.6. It has thus been shown by X-ray diffraction analysis that the oxide fabrication route outlined in Chapter 5 is able to target an x-value by mixing the Ce and Nd nitrate feeds in the desired molar ratio. The lattice parameter has been determined in preparation for future oxide sintering studies where variations in oxygen-to-metal ratio and crystallography may want to be investigated by determining the x-value from the lattice parameter. With the crystallography of the oxide well characterised, future sintering studies can be conducted where the impact of the sintering method on the crystal structure can be assessed.

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CHAPTER 8: CONCLUSIONS AND PROPOSED FUTURE WORK

The fuel development research for the European Space Agency's radioisotope power systems programme is multifaceted with a vast amount of research still to be conducted. The programme has yet to decide:

- The form of americium oxide that will be used as the RPS fuel i.e. whether it will be Am_2O_3 , AmO_2 or an $\text{AmO}_{2-(x/2)}$ phase (where x is a fraction between 0 and 1)³⁰.
- The geometry and aspect ratio of the sintered fuel bodies e.g. pellet height to diameter ratio. It is also possible that the sintered fuel pellets for RPS heat source modules and the radioisotope heater units may have different geometries and aspect ratios.
- The choice of sintering technique to consolidate the oxide fuel powder.

The current ESA chemical flow-sheet creates lath-shaped AmO_2 using an oxalate precipitation and calcination route. In Chapter 2, a literature review of how the variables of an oxalate precipitation process impact the characteristics of oxalate and oxide particles was provided. In particular, cerium, americium and plutonium oxalate precipitation literature were reviewed and the impact of the variables on particle morphology and size was discussed.

In Chapter 3, the spark plasma sintering and cold-press-and-sinter methods were described and compared. The idea that the properties of a sintered pellet such as density are affected by the characteristics of the input powder e.g. size, was introduced. The literature on the SPS and cold-press-and-sinter of CeO_2 and Nd_2O_3 were reviewed. The review highlighted the need for more SPS sintering studies with these materials and found that the CeO_2 SPS studies focussed on using nanometric material. No publicly available literature on the spark plasma sintering nor cold-pressing-and-sintering of lath-shaped micrometric CeO_2 was found. Vickers hardness was one of the few mechanical properties measured and more frequently reported for nuclear oxide materials. Consequently, and because such tests require little material (see Chapter 4), it was decided that compacts

³⁰ $\text{AmO}_{2-(x/2)}$ is more commonly referred to as AmO_{2-X} where X is fraction between 0 and 0.5.

sintered during the course of this study would undergo Vickers hardness tests and the results would be compared to compare a mechanical property of materials prepared with the two techniques. Chapters 2 and 3 highlighted the sheer number of interplaying variables in the oxide synthesis and sintering processes that could have the potential to impact the sintering behaviour of the americium oxide surrogates, and thus impact the resultant sintered pellet properties. They therefore affect the ability to achieve the early ESA requirements of the sintered fuel (see § 2.1 of Chapter 1) e.g. relative densities between 85-90 % and reproducible geometry. The three ESA early fuel development objectives (initially outlined in Chapter 1 in § 2.3) were to:

- 1. Synthesise and characterise surrogates for different americium oxides and establish the effect of varying the synthesis parameters on the particle characteristics, such as shape and size. The key motivation is to be able to create oxide particles with different characteristics without the need for ball-milling the powder. Ball-milling should be avoided for radiological protection reasons. Micron-sized (micrometric) material is therefore targeted to avoid respirable fine production. A first step will be to understand how varying the parameters of the oxalate precipitation process influence the characteristics of the oxalate particles.*
- 2. Compare and assess how surrogates for different americium oxides sinter under different sintering environments. This includes comparing different sintering techniques and assessing, for example, pellet/disc relative density and changes in composition and crystallography. Volume changes associated with crystallographic phase transitions may want to be avoided during sintering as this could, for example, impact densification (see Chapter 5 for further details).*
- 3. Compare the impact of varying the particle characteristics, such as shape and size, of the input surrogate materials on sintered pellet properties e.g. relative density and mechanical integrity.*

In § 1.1 of this chapter, the key conclusions of the three investigations outlined in Chapters 5, 6 and 7 are summarised with their contributions and relevance to the ESA programme highlighted. In particular, references of how this research has contributed to the aforementioned objectives are made. Avenues of future research are also proposed.

1. Key Conclusions and their Contribution to the ESA programme

1.1. The Cerium Neodymium Oxide Solid Solution

As was stated at the start of this chapter, the form of americium oxide for ESA RPSs has yet to be decided. The literature has shown that CeO_2 and Nd_2O_3 can be used as surrogates for AmO_2 and Am_2O_3 owing to similarities in their crystal structures, melting temperatures and thermal expansion coefficients (see Chapters 5 and 6 and the references therein). The ESA programme may require surrogates for cubic $\text{AmO}_{2-(x/2)}$. In Chapter 5, a Ce Nd oxide solid solution, namely a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ phase, with an Ia-3 cubic crystal structure was proposed as a potential surrogate for certain Ia-3 $\text{AmO}_{2-(x/2)}$ oxide phases between x equal to 0.5 and 0.7 i.e. those within the C' phase in the Am-O phase diagram (see Figure 1.5 in Chapter 1).

This research has demonstrated that the proposed continuous oxalate co-precipitation and calcination synthesis process (see Chapter 5) can be used to synthesise $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a targeted x-value with reproducibility. Such a capability will be essential for future sintering trials where a reproducible surrogate oxide feedstock will be required. In the presented study a nominal target of 0.6 was chosen. The x-value of the oxide was targeted by the molar ratio of the cerium(III) nitrates and neodymium(III) nitrates that were dissolved in the nitric acid reagent input feed. Quantitative X-ray fluorescence analysis was used to analyse the cerium and neodymium content in the oxide samples. The results corresponded to an x-value equal to 0.62 for each of the fabricated oxides and the results were independent of the oxalate precipitation temperature used. The result was thus consistent with the nominal target. X-ray diffraction analysis and Raman spectroscopy confirmed that the synthesis process fabricated a material with the target cubic crystal structure (with an Ia-3 space group).

In Chapter 7, the lattice parameter of a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ surrogate that was synthesised using the method outlined in Chapter 5 was determined by the Rietveld refinement analysis of the X-ray diffraction data. This was conducted as the lattice parameter of the material will need to be characterised before future sintering trials with the material are conducted; the second ESA early fuel development objective refers to assessing the crystallographic changes of an oxide during sintering.

Following this, a relationship (see Equation 12 in Chapter 7) developed by Horlait et al. (2011) was used to determine the x-value of the oxide from the lattice parameter. The parameter was consistent with an x-value of ~ 0.6 . The result therefore corroborated with the QXRF result of Chapter 5 and therefore the ability to synthesise a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with a target x-value.

The effect of precipitation temperature on Ce Nd oxalate particle characteristics has also been investigated for the first time; this study contributes to the first of the ESA early fuel development objectives. These results were presented in Chapter 5. Ce Nd oxalate particles with lath and plate-like morphologies were created when precipitated at 25 °C and 60 °C, respectively (see Chapter 5 for the details of the other precipitation variables). The lath particles precipitated at 25 °C were similar to the AmO_2 particles made using the current ESA chemical flow-sheet. Chapter 2 stated that $\text{AmO}_{2-(x/2)}$ powder fabrication would involve exposing the AmO_2 lath-shaped material to a reducing environment. It is reasonable to assume that the lath-shaped Ce Nd oxalate material would maintain its morphology and that it would be a suitable surrogate for lath-shaped $\text{AmO}_{2-(x/2)}$.

The effect of the precipitation temperature on Ce Nd oxalate particle size distribution has also been investigated to contribute to the first ESA early fuel development objective. The Ce Nd oxalate particles precipitated at 25 °C had median sizes that were around 10 μm lower than the median particle sizes of the 60 °C oxalate particles. This result was found regardless of the assumption used for the refractive indices in the optical models.

It is proposed that the calcined oxalates undergo particle size analysis by laser diffraction to see if the calcined 60 °C oxalate material remains larger than the 25 °C material. Specific surface area analysis of the samples should also be conducted to characterise the oxide powder for sintering studies.

This thesis presents a method for synthesising $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with different x-values as a potential surrogate for certain $\text{AmO}_{2-(x/2)}$ phases in preparation for future potential sintering trials. This could include FCC $\text{AmO}_{2-(x/2)}$ phases for x-values up to around 0.4. It does not require specialist equipment unlike $\text{CeO}_{2-(x/2)}$ production, which requires furnaces with reducing environments to reduce CeO_2 to the desired oxygen-to-metal ratios. A practical advantage of the Ce Nd oxalate precipitation method is that it requires

minimal hands-on attendance once started. This makes it ideal for regular surrogate production for sintering trials.

Future research should also involve conducting high temperature X-ray diffraction studies on $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ phases with different x-values (0 to 1) to develop the Ce-Nd-O phase diagram. More data is needed in particular for oxides with x-values close to and equal to 0.6 in order to confirm the suitability of the Ce Nd oxide fabricated in this study as a surrogate for $\text{AmO}_{1.7}$ at high temperature.

Additionally, the literature review in Chapter 5 highlighted that more high temperature X-ray diffraction studies on $\text{AmO}_{2-(x/2)}$ phases for different x-values (0 to 1) are required to develop an Am-O phase diagram with greater certainty. These data are important for understanding phase changes that may occur when sintering americium oxides (the second ESA early fuel development objective).

1.2. The SPS and Cold-Press-and-Sinter Investigations

An investigation to compare the SPS and cold-press-and-sinter of CeO_2 has been conducted. Additionally, Nd_2O_3 spark plasma sintering investigation has also been undertaken. Both of these sintering investigations were described in Chapter 6 and have contributed to the second ESA early fuel development objective. The CeO_2 study was also contributed to the third objective. The key findings of each of these investigations are outlined in the following sections. Future avenues of research to progress and contribute to the ESA surrogate fuel R&D programme are also proposed.

1.2.1. Cerium(IV) Oxide

Chapter 6 reports the first known study on the SPS of micrometric CeO_2 and in particular lath-shaped CeO_2 . Sintering investigations with lath-shaped ceria were conducted as this provided a more representative surrogate for the lath-shaped AmO_2 (Sarsfield et al., 2016).

The cerium (IV) oxide changed colour from pale yellow to different shades of grey when spark plasma sintered. This indicated that the material had reduced (Bevan, 1955). Initial SPS trials used commercially sourced micrometric CeO_2 . Sintering intact discs proved challenging. A two-stage sintering approach was used to try and mitigate the effects of outgassing that were associated with reduction. It was not clear if this measure mitigated disc cracking when the commercial CeO_2 material was sintered. However, a two-stage

process was used to sinter near-net shaped pellets from lath-shaped CeO₂. These pellets were integral.

The ability to SPS integral near-net shaped pellets each with a geometry indicative of a ~3 W_t americium RHU using lath-shaped CeO₂ was demonstrated. However, the pellets evidenced edge fragmentation (chipping), which suggested that SPS was not able and is not able to create such a geometry with reproducibility without further development. The fabrication of a sintered body with a reproducible geometry is a key requirement of the ESA programme.

The spark plasma sintered pellets had relative densities in/near the target range (at around 85 % T.D. each). Despite being integral after initial sintering, the pellets suffered severe fragmentation over the course of 3.5 months and disintegrated. Colour variations across the pellets suggested gradual reoxidation. The longer term structural integrity of the spark plasma sintered near-net shaped pellets differed greatly from the SPS discs, which did not disintegrate. It is possible that the differences in the particle characteristics of the commercially procured and the wet-chemically synthesised (lath-shaped) material had an impact on the reoxidation behaviour and the longer term structural integrity of spark plasma sintered CeO₂. As AmO₂ reduces more readily than CeO₂ (Whiting et al., 2015), it is expected that the SPS of AmO₂ would be even more challenging and similar difficulties associated with disc/pellet cracking may be encountered.

The sintering investigation also involved conducting Vickers hardness tests on the sintered material. With regards to the spark plasma sintered CeO₂ material, a sufficient number of acceptable indents could only be recorded for disc A, which was made using commercially sourced CeO₂. Its hardness was inferior to data reported in the literature for nuclear ceramics, namely UO₂.

This investigation is also the first known public study to cold-press-and-sinter of lath-shaped CeO₂. This was enabled by a collaboration (see acknowledgements). Lath-shaped particles with different sizes and specific surface areas were sintered with the aim of contributing to the third ESA early fuel development objective. The differences in particle characteristics caused a large variation in the sintered disc relative densities and differences in Vickers hardness values. However, no clear relationships between the differences in particle characteristics and these sintered disc properties were found. The

ability to press integral green discs from the various powders differed greatly between them. Some powders could not be successfully pressed into pellets and others had qualitatively better integrity than others. The particle characteristics were therefore greatly influential. Additionally, some sintered discs (2 and 5) suffered delamination. It is possible that this delamination may be associated with the lath morphology and may therefore be concern for sintering lath-shaped AmO_2 in the future.

This comparative sintering investigation has found that the cold-press-and-sinter method can sinter lath-shaped CeO_2 into intact discs that meet the ESA target relative density range. It has also shown that the cold-press-and-sinter method can be used to fabricate sintered CeO_2 discs with superior Vickers hardness than those made by SPS. The hardness values obtained for cold-pressed-and-sintered CeO_2 were also comparable to UO_2 . Cold-press-and-sinter is therefore the preferred sintering method for consolidating CeO_2 . The outlined method does not provide a reducing environment. Therefore the cerium oxide sintered in this way should not have challenges associated with reduction.

It is suggested that CeO_2 particles with non-lath morphology be cold-pressed-and-sintered using the same outlined method to establish the effect on green disc integrity and to see if a change in morphology will mitigate disc delamination. The problem of delamination will need to be resolved in order to improve the longer term structural stability of the discs. Additionally, the impact of a change in particle morphology on the relative densities and Vickers hardness of the sintered discs should be assessed.

1.2.2. Neodymium(III) Oxide

This thesis also presents the first pure Nd_2O_3 SPS investigation. Commercially procured micrometric Nd_2O_3 was sintered. Integral discs and near-net shaped pellets were created without cracks, but they suffered from edge fragmentation (chipping). Spark plasma sintering the material using the current profiles (see Chapter 6) does not provide a reproducible geometry. Future research needs to be conducted to establish how this can be accomplished.

Sintered densities of greater than 95 % T.D. can be achieved by spark plasma sintering Nd_2O_3 at temperatures as low as 1200 °C. A sintering profile, which was based on the results of sintering 20 mm diameter discs, was proposed to enable Nd_2O_3 to be sintered with a relative density within the target range (~85 to 90 % T.D). However, the near-net

shaped pellet that was sintered using this profile had a density of 94 % T.D. The results have shown that the relative density of a sintered pellet not only depends on the sintering profile but also on the geometry and aspect ratio of the pellet/disc. It is therefore proposed that the ESA programme needs to select one or a set of specific geometries/aspect ratios of interest for the sintered fuel form. This will focus the scope of future sintering investigations that aim to sinter surrogates that will meet the early sintered fuel form requirements.

This is the first known study to measure the Vickers hardness of Nd_2O_3 . Although the value is dependent on the sintering method and the specific profile used, the data provides a first indication of the hardness of the Nd_2O_3 . The value was much lower than those of the successfully tested cold-pressed-and-sintered and spark plasma sintered CeO_2 . This may be due to the hygroscopic nature of Nd_2O_3 (it was ground with a water lubricant). The hygroscopicity of the material needs to be considered in future research, particularly if Nd_2O_3 pellets are to be stored for long durations.

Looking forward, Nd_2O_3 particles should be synthesised with a more representative morphology for Am_2O_3 e.g. lath-shaped if Am_2O_3 is to be made by reducing lath-shaped AmO_2 (see the ESA chemical flow-sheet present in Figure 2.2 in Chapter 2). This material should also be used for sintering studies. The effect of different particle characteristics e.g. particle size on sintered pellet properties should be investigated in accordance with third ESA early fuel development objective. The public literature highlighted that there are very few cold-press-and-sinter studies on Nd_2O_3 . A comparative sintering study between the SPS and cold-press-and-sinter of Nd_2O_3 is suggested (to meet ESA objective number 2) to infer how Am_2O_3 may sinter under these environments and therefore to inform the ESA programme on a suitable method for sintering Am_2O_3 .

Finally, it is noted that some americium oxide sintering trials have been conducted more recently as part of the wider ESA RPS fuel development programme. The research suggests (Colle et al., 2017) that future sintering trials will be conducted with Am_2O_3 . Surrogate sintering studies will therefore be required. Fabricating Nd_2O_3 with a range of particle characteristics could be informative to these investigations.

2. A Final Remark

This thesis has presented several investigations with surrogates for americium oxides. The results contribute to the ongoing fuel research and development for the European Space Agency's radioisotope power systems programme. The characteristics of the oxide material will be influential to sintering an integral pellet or disc with the target relative density and with reproducible geometry. The surrogate investigations of this thesis have indeed demonstrated this. They have also highlighted future avenues of research that the programme will need to address as it progresses with the fuel development. More oxalate precipitation experiments to fabricate surrogate oxides with a range of morphologies, sizes and specific surfaces areas should be conducted. The sintering technique and the sintering profile also impact the ability to sinter a pellet/disc that meets the early ESA requirements. Based on the CeO_2 SPS studies, it is proposed that the spark plasma sintering method is an unsuitable method for sintering AmO_2 . In this thesis, it has been highlighted that the geometry and aspect ratio of the sintered fuel needs to be decided to focus the scope of these sintering studies.

The americium oxide fuel development research is multifaceted and expansive. The cost and complexity of this research requires studies with surrogate oxides. These provide indications of how americium oxides can be synthesised and sintered to achieve the required sintered body properties. The fuel development research is likely to take several years. The design of the fuel form will impact the design of the ^{241}Am heater units and modular heat sources for European ^{241}Am RTGs or Stirling generators. One day, a European ^{241}Am radioisotope power system will enable the exploration of the dark regions of the solar system.

APPENDICES

Appendix A

The reader is referred to the referenced studies for full quantitative details of the oxalate precipitation experiments described below in Table A1.

Table A1: illustrates some examples of the results of changing oxalate precipitation experiment variables on oxalate or oxide particle size.

Study	Material	Direct strike/ reverse strike/ continuous	Precipitation Variable		Result	
Li et al. (2009)	Ce(III) oxalate	Continuous	Cerium nitrate concn. (M)	Oxalic acid concn. (M)	Median oxalate particle size (µm)	Distribution Width
			0.02	0.03	59.63	1.725
			0.10	0.15	39.79	1.321
			0.14	0.21	53.05	1.117
Li et al. (2009)	Ce(III) oxalate	Continuous	Mixing rate (RPM)		Median oxalate particle size (µm)	
			200		59.63	
			400		27.82	
			500		49.87	
Rankin and Burney (1974)	Pu(III) oxalate	Direct Strike	Mixing rate (RPM) of 'half' of the oxalate sample whilst digesting.		Median particle sizes of the resultant oxides (µm)	
			500		28	
			2500		17	

Appendix B

Table B1: summarises some of the key trends/findings outlined in the studies reviewed in Chapter 3. The reader is referred to Chapter 3 for further details. Only studies where the effect of the sintering process on relative density, porosity and grain size are summarised.

Sintering Technique	Material	Reference	Trend or Key Finding
Spark plasma sintering	UO ₂	Muta et al. (2013)	- Grain size was unaffected by the SPS conditions. - The small grain size caused by a short sintering time was considered the cause of a higher Vickers hardness value than other data in the literature.
		Ge et al. (2013)	- Pressure applied at lower temperatures had a greater impact to increase sintered relative density than did applying pressure at higher temperatures. - An increase in heating rate resulted in an increase in intra-granular porosity and a decrease inter-granular porosity. - An increase in hold time resulted in an increase in grain size.
		Ge et al. (2014)	- Similar relative densities were achieved by sintering: 1) at a high temperature for a short hold time and 2) at a low temperature for a long hold time. - Grain size depended on the sintered relative density as opposed to the hold time or maximum sintering temperature used.
	CeO ₂	Choi et al. (2010)	- The impact of pressure on sintered relative density was small. - Grain size increased with an increase in sintering temperature. - Sintered relative density increased with an increase in pressure under isothermal conditions. - Under sintering conditions with a zero hold time, the increase in heating rate resulted in an increase in sintered relative density and a decrease in grain size.
		Choi et al. (2012)	- An increase in sintering temperature resulted in an increase in sintered relative density. - Sintered relative density increased with an increase in pressure. - Grain size was not affected by an increase in pressure. - Sintered relative density increased with an increase in hold time but then plateau with a further increase in time.
		Jahromi (2009)	An increase in sintering temperature resulted in an increase in sintered relative density.
Cold-press-and-sinter	CeO ₂	Roleček et al. (2017)	An increase in sintering temperature resulted in an increase in sintered relative density.
		Wang	Flexural strength decreased with an increase in the extent of reduction of CeO₂.

Appendix C

Illustrations of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ Unit Cells

The unit cells of F-type and C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ are illustrated in Figures C.1 a) and C.1 b), respectively.

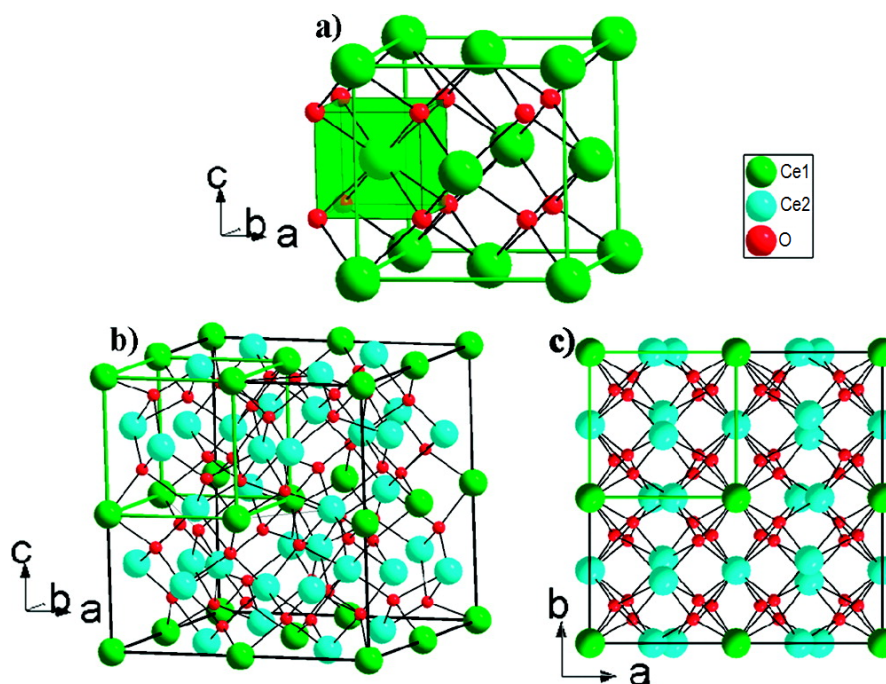


Figure C.1: Illustrates the unit cells of a) F-type and b) C-type $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$. This image was adapted from Horlait et al. (2011).³¹

PXRD

Early trials of oxalate material were made using a similar method outlined at the start of § 2.1 in Chapter 5. Differences included using a shorter precipitation duration and a 150 RPM stirring rate with a 25 °C precipitation temperature. The material was consistently a pink-lilac colour. To confirm that the precipitation procedure was producing oxalates, one of these early samples underwent PXRD. The data were collected from 4 ° to 90 ° 2θ using a 0.5 s step time and a 0.01 ° 2θ step size. The PXRD pattern is illustrated in Figure C.2 for the 2θ angular range of 5 ° to 60 °. The pattern is consistent with those of

³¹ Reprinted with permission from Horlait et al. 2011, *Inorg. Chem.*, **50**, 7150-7161. Copyright (2011) American Chemical Society.

monoclinic (P21/c) rare earth oxalate hydrates, such as cerium (III) oxalate hydrate (PDF 00-020-0268) and neodymium (III) oxalate hydrate (PDF 00-020-0764).

All future made samples (according to the conditions noted in Table 5.3 in Chapter 5) were similar in colour to this early trial material analysed by PXRD. It was assumed that all precipitated samples were similar oxalates. Raman spectroscopy was used to analyse these future samples in order to validate the assumption.

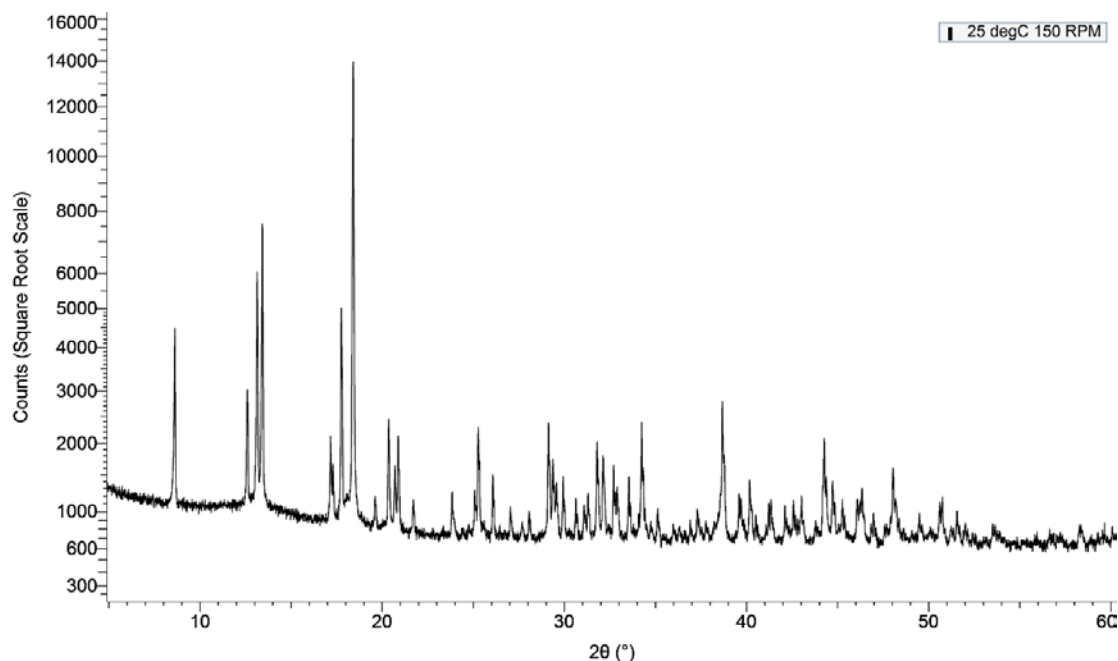


Figure C.2: PXRD pattern of the precipitated material made using similar conditions (25 °C, 150 RPM) to those outlined in Table 5.3 in Chapter 5. The angular range from 5 ° to 60 ° is illustrated.

Raman Spectroscopy

An example of a Raman spectrum taken of a single location in a 60 °C oxalate precipitate (see Table 5.3 in Chapter 5) is shown in Figure C.3. The spectrum is similar and comparable with that of $\text{Ce}_{0.715}\text{Nd}_{0.285}(\text{C}_2\text{O}_4)_{1.5} \cdot 5\text{H}_2\text{O}$ presented by Horlait et al. (2011) in their supporting information. The wavenumber range of 200 to 1800 cm^{-1} is shown in Figure C.3 to aid this comparison. The Raman spectra of the precipitates were thus consistent with Ce Nd (III) oxalate.

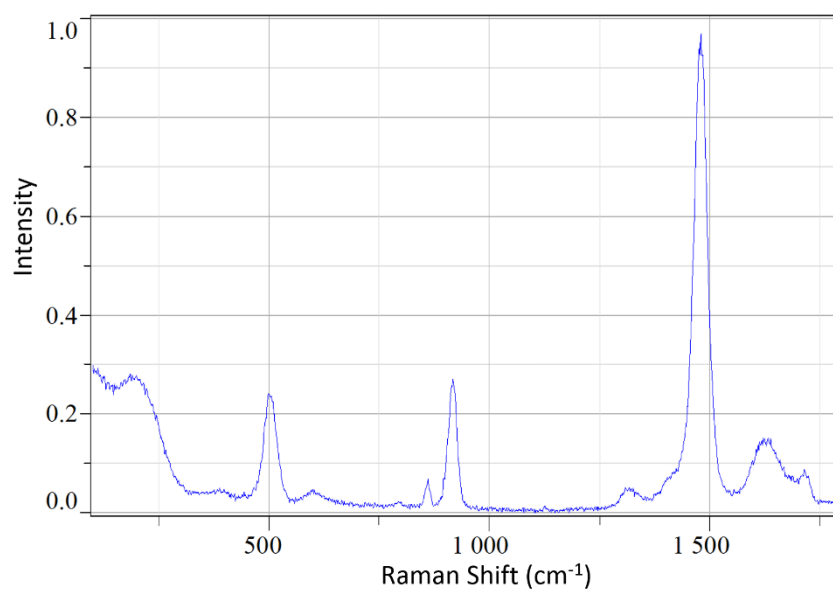


Figure C.3: Raman spectrum of the first 60 °C oxalate sample (made using a 250 RPM mixing rate condition C, which was explained in Chapter 5). Only the wavenumber range from 100 to 1800 cm^{-1} is illustrated to aid comparison with the study by Horlait et al. (2011).

Example of the Gaussian Fit to the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ Pattern used for Estimate Lattice Parameter Estimation

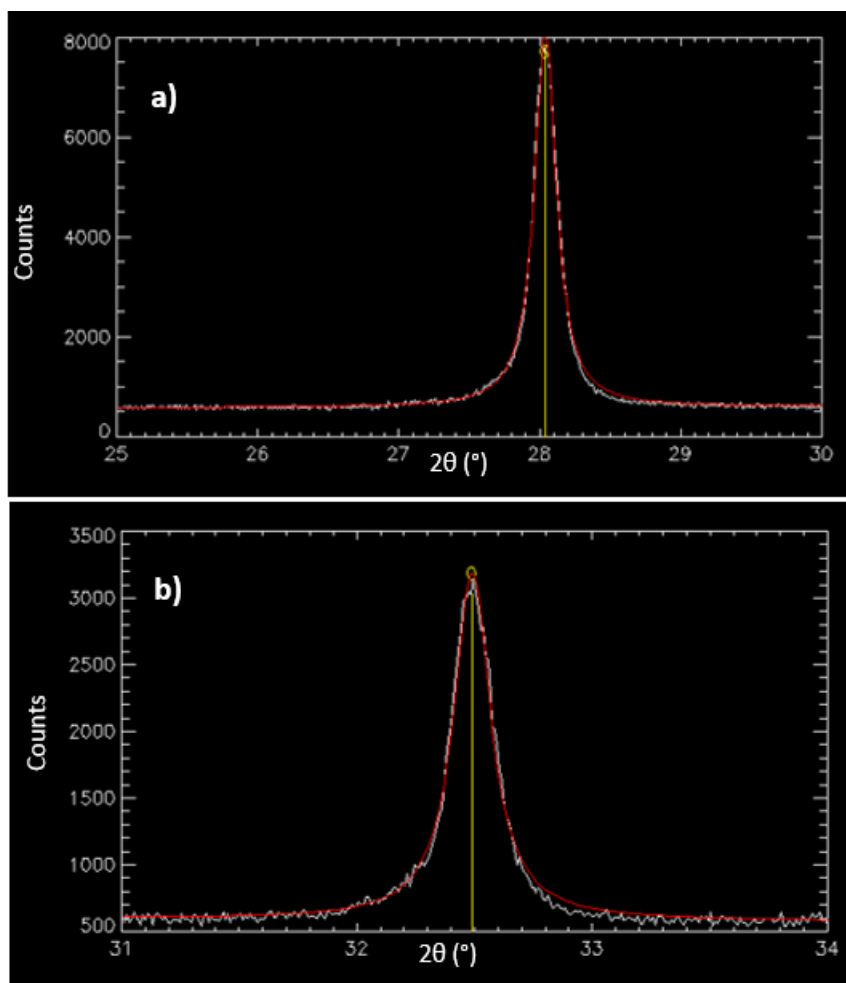


Figure C.4: Examples of the Gaussian fits to the a) (2 2 2) and b) (4 0 0) peaks of the calcined 25 °C oxalate PXRD pattern recorded using scan set b).

Appendix D

Although the diffractometer was equipped with a Ni $\text{CuK}\beta$ filter, it was assessed whether a small unfiltered fraction could have been diffracted by the sample to cause one of the neighbouring peak features depicted in Figure 7.1 in Chapter 7. This was negated as a cause for these features as their peak positions were inconsistent across the pattern. The $\text{CuK}\beta$ contribution was deemed minimal and was not modelled in the analysis.

In an endeavour to establish whether these features were indicative of diffraction from spurious X-rays with different wavelengths in the diffractometer e.g. due to contamination within the instrument, the following exercise was conducted³²:

Let Bragg's law (Equation 3 in Chapter 4) be simplified for n equal to 1 and differentiated with respect to θ to give

$$\frac{d\lambda}{d\theta} = 2d \cos \theta. \quad (1)$$

Its inverse is given by

$$\frac{d\theta}{d\lambda} = \frac{1}{2d \cos \theta}, \quad (2a)$$

which can be approximated by the following

$$\Delta\lambda = 2d \cos \theta \Delta\theta \quad (2b)$$

Consider two X-rays with a fixed wavelength difference ($\Delta\lambda$) e.g. Cu $K\alpha_1$ and $K\alpha_2$. Now consider the diffraction of these X-rays. Let an X-ray diffraction pattern now be considered. Equation 2b shows that in order to maintain the constant $\Delta\lambda$ condition with an increase in θ (or 2θ), the separation of the Cu $K\alpha_1$ and $K\alpha_2$ peaks for a given reflection must vary. There is thus an associated variation in $\Delta\theta$ for each hkl reflection (peak) from the multiple diffracting wavelengths (here, a Cu $K\alpha_{1,2}$ doublet) across the pattern and hence a stretching. Let it be assumed that $\frac{d\theta}{d\lambda}$ is essentially constant over the small 2θ range of a given reflection e.g. in the proximity of a given Cu $K\alpha_{1,2}$ doublet. Then the $\Delta\theta$ for each peak doublet can be estimated by assuming a value θ for the peak e.g. that for the Cu $K\alpha_1$. This $\Delta\theta$ correction can then be applied to each data point that is in the vicinity of the doublet. If they are then overlaid on a single plot with the Cu $K\alpha_1$ positions aligned, it would be expected that the Cu $K\alpha_2$ peaks would align if the constant $\Delta\lambda$ condition should be maintained. This method was applied to a number of diffraction peaks of the SRM corundum XRD pattern and, as expected, the positions of the Cu $K\alpha_2$ were essentially aligned as shown in Figure D.1. If the 'neighbouring features' depicted in

³² The exercise was suggested following a discussion with Dr. G. Hansford.

Figure 7.1 in Chapter 7 were due to diffraction from extra wavelength contributions, then these features would have been expected to align in the plot. However, as the alignment was not consistent between peaks, it was concluded that these features were not caused by diffraction from additional wavelength contributions. The cause for these could not be established and therefore could not be modelled in MAUD.

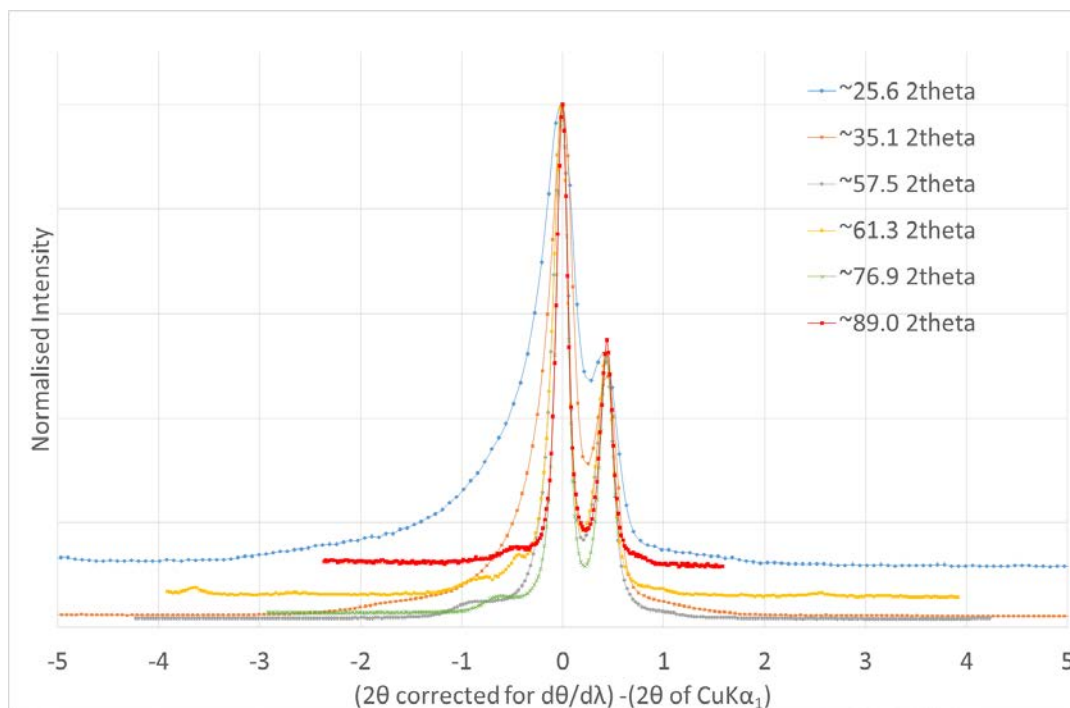


Figure D.1: Illustrates how the Cu $K\alpha_1$ and $K\alpha_2$ peaks align once a correction for their separation based on Equations 2a and 2b is applied owing to a constant $\Delta\lambda$. However, the ‘neighbouring features’ do not align upon applying this correction indicating $\Delta\lambda$ is not maintained relative to Cu $K\alpha_1$. This indicates that they are not due to diffraction of other wavelengths.

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PUBLICATIONS

The following list also includes journal articles that are in preparation for submission. It is indicated in italics when a chapter is based on a journal article.

1. E. J. Watkinson, R. M. Ambrosi, H. R. Williams, M. J. Sarsfield, K. Stephenson, D. P. Weston, N. Marsh & C. Haidon, (2017) Cerium Neodymium Oxide Solid Solution Synthesis as a Potential Analogue for Substoichiometric AmO₂ for Radioisotope Power Systems. *Journal of Nuclear Materials*, 486, p. 308-322.
<http://doi.org/10.1016/j.jnucmat.2017.01.011> (*This is the basis for Chapter 5.*).
2. E. J. Watkinson, R. M. Ambrosi, D. P. Kramer, H. R. Williams, M. J. Reece, K. Chen, M. J. Sarsfield, C. D. Barklay, H. Fenwick, D. P. Weston and K. Stephenson, (2017). Sintering Trials of Analogues of Americium Oxides for Radioisotope Power Systems. *Journal of Nuclear Materials*, 491, p. 18-30.
<http://doi.org/10.1016/j.jnucmat.2017.04.028> (*This is the basis for Chapter 6.*).
3. E. J. Watkinson, D. Chateigner, R M. Ambrosi, H. R. Williams, C. H. Haidon, K. Stephenson et al., Detailed X-ray Diffraction Analysis of Ce_{1-x}Nd_xO_{2-(x/2)} as a Surrogate for Substoichiometric Americium Oxide (This article is under preparation. *This is the basis for some of Chapter 7.*).

Although not presented in this thesis, there has been an ongoing collaborative study with Dr C. E. Whiting at University of Dayton Research Institute (Dayton, OH, USA), to model the effect of different environments on the reduction of CeO₂, AmO₂ and PuO₂ in the context of radioisotope thermoelectric generators. This work has been presented at the Nuclear and Emerging Technologies for Space 2015 and 2016 conferences and will be prepared for publication in 2017.

GLOSSARY

Acicular shape: this term is often used to describe crystals that are needle-like (Merriam-Webster, 2017).

Aging/digestion time: the duration over which the crystal is permitted to grow.

Analyte: the material/sample of interest to undergo some measurement for later analysis.

Dendrite: “a tree-like crystal” (Glicksman, 2004).

Differential sintering: according to Kong et al. (2015), this term means that “different regions of the bodies have different densification behaviors, due to inhomogeneity.”

Direct strike: in the context of this thesis it refers to when oxalic acid is added to the metal nitrate solution.

General Purpose Heat Source (GPHS): the module based heat source used in modern U.S. radioisotope thermoelectric generators. The reader is referred to Chapter 1 for more details.

Green body/pellet/disc: is term used in the nuclear industry to describe a cold pressed compact. The compact has not yet been sintered.

Lath-shaped particle: an illustration of this morphology can be found in Figure 1.6 of Chapter 1. This term has also been used to describe some of the Pu(III) oxalate particles as a precursor to PuO₂ production for fabricating GPHS pellets (Borland et al., 2009).

Mother Liquor: “a residual liquid resulting from crystallization and remaining after the substances that readily or regularly crystallize have been removed” (Merriam-Webster, 2017a).

Multiple scattering: The following is based on an explanation by NIST et al. (2001): multiple scattering describes when the light scattered from a particle is then scattered by another particle. The concentration of particles in a given volume therefore affects whether multiple scattering occurs and each laser diffraction instrument manufacturer suggests an obscuration range to enable sufficient signal for detection but which should minimise multiple scattering. The obscuration level describes the “extent of attenuation

of incident beam intensity due to presence of particles” (NIST et al., 2001). It is important to input (e.g. via pipette) the sample to ensure consistent obscuration values as this can affect the results, but the extent of this depends on the sample.

Nanometric: a term used to describe an object that has a size that is on the nanometre scale.

Near-net shape: near-net shape refers to the ability of a process to manufacture a powder into a shape that is close to the final, or ‘net’, required shape (Mercury Centre, 2017).

Nucleation: “the series of atomic or molecular processes by which the atoms or molecules of a reactant phase rearrange into a cluster of the product phase large enough as to have the ability to grow irreversibly to a macroscopically large size” (Cubillas and Anderson, 2010). They note the cluster is the nucleus.

Optical model: In particle size analysis by laser diffraction the optical model specifies the algorithm the instrument uses to interpret the scattered light intensity to infer a particle size distribution. Commercial instruments allow an operator to choose a model based on Mie theory or the Fraunhofer diffraction approximation.

PIDS method: Please see the acronym list and please also see § 2.5 in Chapter 4 for an explanation.

Precipitation: a two part process that comprises a nucleation stage and growth stage, which impact particle morphology and size (Sarsfield et al., 2015, Bertrand-Andrieu, 2004).

Rayleigh scattering: Please see § 2.3 in Chapter 4 for an explanation.

Reagent: an input material for a chemical reaction.

Reduce: to remove oxygen from a material or increase the negative charge. Although there are other definitions of reduction, the aforementioned definition is the most relevant to the context for this thesis.

Relative density: the measured density of a material divided by its theoretical density. The ratio is often presented as a percentage.

Respirable fine: a 1974 study by Rankin and Burney (1974) suggested that particles less than 4 μm in size were considered respirable fines, but more recent literature suggests that producing particles greater 10 μm is desirable (Borland et al., 2008). This suggests that particles smaller than 10 μm are considered respirable.

Reverse strike: in the context of this thesis it refers to when the metal nitrate solution is added to oxalic acid solution.

Rietveld Refinement: Please see § 2.2 of Chapter 4 for an introductory explanation.

Sinter(ing): the reader is referred to § 2 of Chapter 3 for a detailed explanation. In the context of this thesis, it is a method used to consolidate a powder into a structure by applying heat (together with current and pressure in the case of spark plasma sintering).

Specific electrical power (often shorted to specific power): the electrical power generated in Watts per kilogram of the total power system.

Specific surface area: the surface area per unit mass. Its units are typically $\text{m}^2 \text{g}^{-1}$. It is measured using the Brunauer–Emmett–Teller (BET).

Spherulite: is “a usually spherical crystalline body of radiating crystal fibers” (Merriam-Webster, 2017b).

Thermal etching: etching allows the microstructure of a material (ceramics in this thesis) to be more easily observed and “enhances” features such as grain boundaries (Della Bona, 2005). Geels et al. (2007) describe that thermal etching involves heating the material at high temperature. The result is that “grooves are formed in the grain boundaries/phase boundaries and grain surfaces are curved” (Geels et al., 2007).