Cerium Neodymium Oxide Solid Solution Synthesis as a Potential Analogue for Substoichiometric AmO₂ for Radioisotope Power Systems

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10 Abstract

- 11 The European Space Agency (ESA) is sponsoring a research programme on the development of
- 12 americium oxides for radioisotope generators and heater units. Cubic AmO_{2-(x/2)} with an O/Am ratio
- between 1.65 and 1.75 is a potentially suitable compound for pellet sintering. C-type (Ia-3) Ce₁₋
- 14 $_xNd_xO_{2-(x/2)}$ oxides with 0.5 < x < 0.7 could be used as a surrogate for some Ia-3 AmO_{2-(x/2)}. A new Ce₁₋
- $15 _xNd_xO_{2-(x/2)}$ production process has been investigated where a nominally selected x value of 0.6 was
- 16 targeted: Ce and Nd nitrates and oxalic acid were added drop-wise into a vessel, where they
- 17 continuously reacted to create oxalate precipitates. The effect of temperature (25°C, 60°C) of the
- 18 reactants (mixed at 250 revolutions per minute) on oxalate particle shape and size were
- 19 investigated. Oxalates were calcined at 900 °C to produce oxide particles. Oxalate particle properties
- were characterised as these are expected to influence oxides particle properties and fuel pelletsintering.

22 1 Introduction

- 23 Radioisotope Power Systems (RPS) enable exploration of some of the more challenging
- environments in the solar system such as deep space. These power systems are independent of the
- 25 local solar intensity in contrast to solar power systems. A radioisotope thermometric generator
- 26 (RTG) is one type of RPS that converts decay heat from a radioisotope into electricity. RPS have
- 27 heritage dating back to the 1960s [1]. The versatility of these systems has enabled missions such as
- 28 NASA's Mars Science Laboratory that has its *Curiosity* rover powered by a Multi-Mission
- 29 Radioisotope Thermoelectric Generator (MMRTG) [1]. The General Purpose Heat Source RTGs,
- 30 which were flown on Cassini, and more modern USA RTGs such as the MMRTG, comprise modular
- 31 heat sources known as General Purpose Heat Sources (GPHS). These contain ²³⁸PuO₂ pellets
- 32 surrounded by multiple containment layers (including cladding, impact and ablative layers) that
- provide protection against a potential launch accident and Earth re-entry scenarios.
- 34 Since the U.S. production of ²³⁸Pu was halted in the late 1980s, the dwindling stock available for
- 35 NASA science missions has threatened to limit the number of RPS-powered missions [2]. A planned
- 36 re-start of production will be on a small scale and ²³⁸Pu will remain a very scarce resource for the
- 37 foreseeable future [3].
- 38 In 2008, the European Space Agency (ESA) began a research and development programme into the
- 39 production of a European RPS [4-7]. Americium-241 (²⁴¹Am) has been selected as the RPS fuel
- 40 choice. It was identified as a potentially viable, and affordable, alternative for Europe [4] despite its
- 41 lower specific thermal power than ²³⁸Pu [4,8]. Research into americium oxide production and

- 42 processing as well as into the development of different RPS technologies is being pursued in the
- 43 programme. Such technologies include RTGs [5], Stirling Generators [4], and Radioisotope Heater
 44 Unite (RHUE)
- 44 Units (RHUs).
- 45 Research into different forms of americium oxide is ongoing to decide which chemical form of the
- 46 fuel should be used. There are a number of feasible solid oxides ranging from americium
- 47 sesquioxide (Am₂O₃), which has an oxygen to metal ratio of 1.5, through to americium dioxide
- 48 (AmO₂), which has an oxygen to metal ratio of 2.0. The intermediary phases can be described as
- 49 AmO_{2-X} phases where X ranges from 0.5 to 0. According to the phase diagram by Thiriet et al. [9],
- 50 which is illustrated in Figure 1, Am₂O₃ undergoes phase changes between cubic and hexagonal
- 51 crystallographic forms. Thus depending on the temperatures used during sintering trials, there is the 52 potential for volume changes, which will affect sintering. Chikalla et al. [10] recorded the
- dissociation pressure isotherms for AmO_2 at temperatures between 1139 K and 1455 K. The data
- showed the tendency for AmO_2 to reduce to AmO_{2-x} even under pressures slightly under 1 atm of O_2
- 55 [10].

56 **1.1 Rationale: the ESA Radioisotope Power Systems Programme**

- 57 Am oxides will be produced via an oxalate precipitation and a thermal decomposition (calcination)
- route, where an Am nitrate feed would provide the input to the oxalate precipitation stage. The use
- of an Am nitrate feed is a consequence of the extraction approach used to separate Am (a decay
- 60 product) from separated and stored Pu.
- The fuel will need to be in a form that can be integrated easily into an RPS system. Thus a good
- 62 understanding of the chemical and physical properties of the raw materials, their sinterability and
- 63 the mechanical properties of the sintered products needs to be established and will be necessary for
- 64 the development of a safety framework for European radioisotope power systems. The ability to
- sinter americium oxides into pellets or discs with, for example, high relative density as well as
- 66 mechanical and chemical stability, is an essential part of the ESA-funded programme. There are a
- 67 limited number of experimental investigations on americium oxides in the literature. A wide range
- of experiments will be required. Investigations with suitable surrogate materials are valuable to
 minimise the number of experiments with highly radioactive americium. Three objectives of this
- 70 ESA-funded programme are to:
- 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. A first step will be to understand how varying the parameters of the oxalate
 precipitation process influences the characteristics of the oxalate particles.
- Compare and assess how surrogates for different americium oxides sinter under different
 sintering environments. This will include assessing, for example, pellet/disc relative density
 and changes in composition and crystallography.
- 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.

81 **1.2** Surrogates for Americium Oxides

- 82 Neodymium (III) oxide (Nd_2O_3) and cerium (IV) oxide (CeO_2) are reasonable surrogates for Am_2O_3
- 83 and AmO₂, respectively, depending on the property being assessed. For example, Table 1 shows that

- Nd_2O_3 and CeO_2 can be considered as a 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
- 86 (0.975 Å and 0.983 Å, respectively [11]), the phase transition temperatures, the melting
- 87 temperatures and the coordination numbers associated with each of their crystallographic phases
- 88 e.g. cubic and hexagonal. CeO_2 and AmO_2 have similar cationic radii (0.97 Å and 0.95 Å, respectively)
- [12]. Zinkevich et al. [13] reported a number of values for the melting point of CeO₂ according to
 various literature reviews and research papers e.g. they note the lowest noted value was measured
- 91 by Mordovin et al. [14] to be 2670 K. Zinkevich et al. [13] preferred to use 3000 ± 20 K [15] in their
- 92 Ce-O thermodynamic modelling study as it stated an uncertainty. Thus there is some debate
- 93 regarding its melting temperature. AmO₂ is likely to have a melting point at around 2448 K [16]. This
- 94 discrepancy is acceptable as the surrogate materials will not be sintered at temperatures as high as
- 95 these.
- 96 Volume changes associated with crystallographic phase transitions may want to be avoided during
- 97 sintering. In the context of the ESA programme, it is essential that intact americium oxide discs or
- 98 pellets can be created with reproducible geometry. Thus, such volume changes could make it
- 99 difficult to densify discs or pellets and potentially cause cracking during the fabrication process. Such
- 100 effects should also be avoided during integration in RTG systems or in accident scenarios such as
- 101 launch pad fires or earth re-entry (to name a few), where structural integrity of the pellet or pellets
- 102 is an important consideration for the safety case.
- 103 The phase diagram (see Figure 1) developed by Thiriet et al. [9] shows that AmO₂ and a number of
- substoichiometric americium oxides, AmO_{2-X}, are cubic (unlike Am₂O₃) 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 AmO_{2-x} phase that remains cubic
- with a variation in temperature. A single cubic phase crystal with an O/Am ratio between 1.65 and
- 108 1.75 has been chosen as a preferred starting point. Intermediary oxidation states of americium
- 109 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 et al. [17] has
- gaseous environments, such as hydrogen, to provide reducing environments provided some insight into how this could be achieved.

113 **1.2.1** 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} can be described by a solid solution between the $AmO_{1.5}$ and
- 115 AmO_2 end-species, even though Thiriet et al. [9] stated that $Am_{5/4}O_2$ -AmO₂ may also be valid. The
- 116 AmO_{2-X} crystal structure can be described by the replacement of Am^{4+} ions in the AmO_2 crystal with
- 117 Am^{3+} ions, where half of an oxygen vacancy is introduced each time to ensure charge conservation
- 118 [18]. This has also been described by $\operatorname{Am}_{1-x}^{V}\operatorname{Am}_{x}^{U}O_{2-(x/2)}$, or $\operatorname{Am}O_{2-(x/2)}$ for shorthand, where the
- 119 commonly referred to 'X' of AmO_{2-X} is equal to x/2. The x ranges from 1 ($AmO_{1.5}$) to 0 (AmO_2). The
- 120 $AmO_{2-(x/2)}$ notation is used in this study.
- 121 Although there are surrogate materials for AmO₂ and Am₂O₃, there is nothing similar for the AmO₂.
- 122 (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
- 126 AmO_{1.65} and AmO_{1.75} here.

- 127 Horlait et al. [19] explained (from information provided by Ikuma et al. [20]) how the face centred
- 128 cubic (FCC) CeO₂ structure (Fm-3m), which is called F-type, is doped with neodymium to form a solid solution: the Nd³⁺ ions replace Ce⁴⁺ ions and half of an oxygen vacancy is produced randomly within
- 129
- 130 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 la-3
- 131 132 superstructure (often called C-type), which has a unit cell volume eight times as large as that of the
- 133 F-type structure. For solid solutions with even larger Nd content, surplus hexagonal Nd_2O_3 is found
- 134 to be present in addition to the solid solution. Horlait et al. [19] noted that the synthesis method
- 135 affects the range of x values for each crystal phase of the Ce1-xNdxO2-(x/2) system at room
- 136 temperature. The results of their investigation are outlined in Table 2.
- 137 A literature review found that an extensive phase diagram of the CeO₂-Nd₂O₃ system at different
- elevated temperatures does not exist. The only known phase diagram is presented by Pieczulewski 138
- 139 et al. [21] and comprises only a few data points. Nonetheless, the phase transitions at room
- 140 temperature are well understood as described in the review by Horlait et al. [19].
- 141 In the context of obtaining a potentially suitable surrogate for a single cubic americium oxide phase
- 142 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
- 143 considered. According to the AmO₂-Am₂O₃ phase diagram shown in Figure 1 [9], the only single
- 144 cubic phases that exist between $AmO_{1.65}$ and $AmO_{1.75}$ are either Fm-3m or Ia-3 in structure, which
- 145 they label as α and C', respectively. As most of the oxides ranging from Ce_{0.3}Nd_{0.7}O_{1.65} to
- 146 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
- 147 potential surrogates for these Ia-3 (C') Am oxides. However, as stated earlier, the synthesis method
- 148 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 closer to x equal to 149
- 150 0.7 [19].
- 151 The C' Am oxide phase (AmO_{1.5+ δ}) is noted in a number of sources but different notations are used.
- Thiriet et al. [9] say its region in the phase diagram is often incorrectly drawn in other studies. Their 152
- 153 diagram shows it lies in a region between around AmO_{1.60} and AmO_{1.69} depending on the
- 154 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 1), as is shown for the 155
- 156 C' phase, as well as at low temperatures where data are limited [22]. Thiriet et al. [9] provide further 157 details of the phase diagram, as well as a review of past experimental work with Am oxides. Sari et
- al. [17] assumed the lower limit of the C' (Ia-3) phase to be around $AmO_{1.62}$ with an upper limit of 158
- 159 AmO_{1.68}. This was estimated based on their differential thermal analyses and XRD data. Nishi et al.
- 160 [23] created AmO_{1.73 ± 0.03}, which comprised two body centred cubic phases with lattice parameters
- 161 of 10.97 Å and 10.92 Å. Lebreton et al. [24] 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) $Am_2O_{3+\Delta}$ phase that has a 162
- 163 lattice parameter equal to twice that of Fm-3m $AmO_{2-\Delta}$ [24].
- Sari et al. [17] state that the lattice parameter data recorded by Chikalla et al. [25] varied abruptly as 164
- 165 O/Am ratio approached AmO_{1.67}. The compositions for which either C or C' (both were inferred to be
- 166 Ia-3 phases) was the only phase, or the dominant phase, were $AmO_{1.616}$ through to $AmO_{1.713}$, which
- were all made under He at 800/850/860 °C [25]. However, the trend at other temperatures is 167
- 168 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 169
- 170 Chikalla et al. [25]) but some were mixed phases. Ce_{0.27}Nd_{0.73}O_{1.635} has a lattice parameter of
- 171 11.0536(4) Å, which decreased to 10.9982 (26) Å for Ce_{0.5}Nd_{0.5}O_{1.75} according to Horlait et al. [19].

- 172 There is the potential for Ia-3 $Ce^{|V_{1-x}|}Nd^{|||}_{x}O_{2-(x/2)}$ to be a crystallographic surrogate for Ia-3 AmO_{2-(x/2)}
- 173 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 $Ce^{IV}_{1-x}Nd^{III}_{x}O_{2-(x/2)}$ is not understood at
- 176 elevated temperatures.

177 1.3 Study Objectives

- 178 The aim of the study reported herein is to demonstrate and evaluate the use of an oxalate
- 179 precipitation and calcination based process to create $Ce^{|V|}_{1-x}Nd^{|||}_{x}O_{2-(x/2)}$ as a candidate surrogate for 180 some Ia-3 AmO_{2-(x/2)} phases. The objectives of this study were to:
- Understand how varying the temperature of the oxalate precipitation process affects the
 shape and size of the oxalate particles.
- Determine whether Ce_{1-x}Nd_xO_{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.
- Determine if the Nd/[Ce + 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.
- 193 An x value of 0.60 was nominally targeted in this study.
- 194 Although the production of $Ce_{1-x}Nd_xO_{2-(x/2)}$ system has been explored in the past by solid state routes
- e.g. by Hong et al. [26], and by wet synthesis routes such as by Higashi et al. [27] and Horlait et al.
- 196 [19], 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. [27] added a nitrate mixture
- 198 to oxalic acid to create a different $Ce_{1-x}Nd_xO_{2-(x/2)}$ oxide namely, Fm-3m $Ce_{0.8}Nd_{0.2}O_{1.9}$. Although the
- synthesis of Ce_{0.4}Nd_{0.6}O_{1.7} has been targeted by Horlait et al. [19] using a wet-synthesis oxalate
- 200 precipitation route, they reacted a metal chloride mixture with excess oxalic acid and did so by
- 201 pouring the chloride mixture into the oxalic acid.
- 202 Secondly, this is the first known study to have investigated the influence of the oxalate precipitation
- 203 temperature on Ce Nd oxalate particle properties. It is also the first known investigation to use a
- 204 method that continuously co-precipitates and filters the Ce Nd oxalates (from the mother liquor)
- 205 over several hours. It thus offers a simple co-precipitation method.

206 2 Material Synthesis

207 2.1 Oxalate Precipitation

A solution comprising Ce(III) nitrate and Nd(III) nitrate with a total lanthanide concentration of

- 209 0.0104 M in 0.2 M nitric acid and a 0.68 M oxalic acid solution were fed continuously into a vessel.
- 210 The reaction vessel was designed to allow continuous co-precipitation of the reaction products and
- sat partially within a temperature controlled water bath as illustrated in Figure 2. The water was

- circulated through an integral water jacket on the reaction vessel to ensure uniform temperature.
- 213 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,
- 215 STREM Chemicals UK) were measured under a nitrogen atmosphere to limit water absorption. The
- 216 masses were measured to ensure a molar ratio of Nd/[Ce + Nd] of 0.6, which was expected to target
- an x value of 0.6 in the final oxide (Higashi et al. [27] mixed their metal nitrates in a 0.2 molar ratio
 to target the production Ce_{0.8}Nd_{0.2}O_{1.9}). The temperature of the reaction was controlled. The
- 219 precipitates were continuously filtered through a 0.45 μm Millipore membrane. After several hours
- of co-precipitation, three vials were used to collect outflowing precipitate (suspended in the mother
- liquor) from the vessel outlet (before it reached the filter) for particle size analysis. The filtered
- 222 material was rinsed with water and dried in an oven at 100 °C for a day.
- 223 Samples were precipitated at 25 °C and 60 °C (see Table 3). Two investigations were conducted to 224 assess:
- 1. The effect of reaction temperature on oxalate particle morphology.
- 226 2. The effect of reaction temperature on the particle size.
- 227 Three experiments were conducted per condition set outlined in Table 3 to assess the
- reproducibility of the method and of the samples. This resulted in three batches of material being
- 229 made per condition set.

230 2.2 Calcination

- 231 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 cooling process was more gradual and the system was left to cool overnight.
- 234 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
- 236 batches in total (three were calcined 25 °C oxalates and three were calcined 60 °C oxalates).

237 3 Analytical Methods

238 **3.1** Powder X-ray Diffraction (PXRD)

- 239 Data were acquired using CuKα 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
- 241 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 A.
- 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 3). Diffraction patterns were recorded using the followingparameters:
- Scan set a) angular range: 4° to 90° 2θ; step size: 0.01° 2θ; count time: 0.5 seconds per step.
- Scan set b) angular range: 18 to 52° 2θ; step size: 0.01° 2θ; count time: 5.0 seconds per step.

The ICDD database and other literature were consulted during phase analysis [19, 20]. 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) $Ce_{1-x}Nd_xO_{2-(x/2)}$ by improving the signal to noise ratio. According to PDF 04-013-6624, which is the PDF card of C-type $Ce_{0.5}Nd_{0.5}O_{1.75}$, these peaks were the (2 1 1), (4 1 1), (3 3 2) and (1 3 4) peaks.

254 **3.2 Raman Spectroscopy**

255 Data were acquired with a Renishaw Invia Raman microscope under the extended regime. A 50% 256 filter was used to reduce sample heating. Cosmic rays were automatically removed from the data 257 during acquisition. Sections of the samples were stored and transported in glass vials prior to Raman 258 analysis. Each sample was placed, crushed and had its surface flattened in a sample holder. A 10 s 259 dwell time was used and data were acquired over 5 accumulations per sample. Each spectrum was 260 normalised to the maximum recorded intensity and the background was removed. The oxalate 261 precipitates made using the two different temperatures (see Table 3) were analysed using a 514 nm He-Ne laser (see Appendix A for details). The three calcined 25 °C oxalate precipitate batches and 262 263 the three calcined 60 °C oxalate precipitate batches (see Table 3) were analysed using a 633 nm 264 wavelength laser to establish if there was evidence of the structure of C-type $Ce_{1-x}Nd_xO_{2-(x/2)}$. One sample was taken from each batch for analysis and multiple locations were analysed. The spectra 265 were acquired at 50x magnification. The 'laser diameter' was around 1 μ m for the 50x objective. The 266 267 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).
- 269 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.
- 272 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)" states the number of data points maxima can
- be separated by. These first estimates of peak positions were inspected and peaks those that were not clearly evident in the spectra were not considered. The peaks were then fitted using a
- 275 Intercently evident in the spectra were not considered. The peaks were then inted using a
 276 Levenberg-Marquart fitting procedure. The overall fitted curve and the deconvolved peaks were
- 277 inspected qualitatively for goodness of fit.

278 **3.3 Quantitative X-ray Fluorescence (XRF)**

- 279 The calcined oxalate samples underwent quantitative X-ray fluorescence analysis using a PANalytical
- 280 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 [28, 29]. It enables repeatable sample
- 283 preparation by creating homogenous samples that negate mineralogical differences that can affect
- the measured line intensities. The method used required 0.1 g of sample per fused bead.
- 285 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 3). Different
- 287 predefined masses of CeO_2 and Nd_2O_3 were measured to make calibration fusion beads with
- $288 \qquad different wt\% \ of \ CeO_2 \ and \ Nd_2O_3. \ These \ were \ then \ analysed \ where \ the \ intensities \ of \ the \ isolated \ Ce$
- 289 $L_{\alpha 1}$ (4.8402 KeV) and the Nd $L_{\beta 1}$ (5.7216 KeV) lines were measured and corrected for matrix effects
- and background. The matrix was stated to be CeO_2 and Nd_2O_3 as the Ce and Nd ions in the fusion
- 291 melt would have fully oxidised.

- 292 Each calcined oxalate precipitate batch (see § 2.2) underwent quantitative XRF analysis to assess the
- 293 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 CeO_2 and Nd_2O_3 matrix was assumed. The software corrected the measured intensities for background, system drift, as well as matrix effects, as described by Jenkins et al. [28] and Jenkins
- [29], and the CeO_2 and Nd_2O_3 concentrations by mass were calculated using the calibration curves.
- 298 Post-analysis involved converting these to Ce molar % and Nd molar % concentrations (using the
- atomic weights of Ce, Nd, CeO₂ and Nd₂O₃ according to NIST [30]) to then calculate the molar ratio
- 300 Nd/[Ce + Nd]. Note an additional factor of two was used to calculate the Nd molar % to account for
- 301 there being two Nd atoms per Nd_2O_3 .

302 3.4 Scanning Electron Microscopy (SEM)

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

306 3.5 Particle Size Analysis

307 The particle size distributions (including Polarization Intensity Differential Scattering, PIDS) of the Ce

- 308 Nd oxalate suspensions were analysed using a Beckman LS Coulter 230 with the Variable Speed Fluid
- 309 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.
- 311 Three batches of material were made (see § 2.1) using a 25 °C precipitation temperature and 312 another three were made at 60 °C (see Table 3). Three vials of suspended precipitates were 313 collected per batch made (see section § 2.1). These suspensions were deemed representative of the 314 oxalates made throughout the synthesis process e.g. hours before, as the experimental conditions 315 (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 316 317 25 °C and another 9 for precipitates made at 60 °C. The samples made at 60 °C were analysed first 318 and data sets 1-3 were used to validate the material re-suspension method by vial flipping. A pipette 319 was used to collect suspended material for analysis. Data sets 4-5 were used to establish the time 320 needed for the samples to circulate around the system. The particle size distribution (PSD) of data 321 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 322 323 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.
- 327 The apparatus used a 750 nm light source to analyse particles with equivalent spherical diameters
- between 0.04 μm and 2000 μm [31]. Under the PIDS regime, it used three polarised light sources
- 329 (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
- $\,$ 331 $\,$ $\,$ particles typically had dimensions between 1 and 50 $\mu m.$ Consequently, as the particle diameters $\,$
- were not much greater than the wavelength of the incident radiation [32], a Fraunhofer
- approximation based optical model was discounted and a model based on Mie theory was chosen.
- 334 This required the real and imaginary components of the refractive indices of the material to be

- specified as well of that of the suspension fluid. The default value for water (1.332) was specified forthe latter.
- 337 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 [33]: 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
- 341 refractive index of 1.61 and 'Ce Oxalate Min' assumed a real refractive index of 1.47. Wylie did not
- 342 specify the wavelength of the radiation used to calculate these indices nor their imaginary
- 343 components [33]. Ideally a refractive index obtained using a similar wavelength to that of the LS
- 344 Coulter 230 should have been specified.
- 345 Generally, it is well known that the definition of the optical model can have an effect on the
- resultant PSD [32, 34] 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 UO₂, despite its different (cubic) crystal structure. The
- optical model was denoted as 'UO₂' and used 2.42 and 0.015 for the real and imaginary refractive
 index components, respectively [35].
- _____

352 **4** <u>Results</u>

353 4.1 Oxide Material Characterisation

354 **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
- 357 result was also independent of whether the calcined samples were created from oxalates that were
- 358 made at 25 °C or at 60 °C (see Table 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
- 360 composition is essential for establishing a synthesis method where samples may be required for
- 361 multiple investigations.
- 362 The target of 0.6 has been achieved with a ~3% discrepancy for all fused beads. A small deviation is
- 363 not unforeseen e.g. Horlait et al. [19] found small deviations between their expected x values and
- 364 those of their oxides as determined by energy-dispersive X-ray spectroscopy. They attributed it to
- 365 measurement uncertainty and the hygroscopic nature of their chlorides. Ce and Nd nitrate
- 366 hexahydrates are slightly hygroscopic and are thus a potential contributing cause for the
- 367 discrepancy in this study. Efforts were made to contain the material and to generally open it in dry 368 environments.
- 369 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 [36]. The net number of counts in 40 s

- was 5855444, 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
- 380 curves. This thus may have impacted the wt% values determined for the $Ce_{1-x}Nd_xO_{2-(x/2)}$ analysed
- 381 oxides.
- 382 Two beads with approximately 60 wt% Nd₂O₃ and 40% wt CeO₂ (each relative to the total CeO₂ and
- 383 Nd₂O₃ sample content) were used in the calibration process. These were later measured as
- 384 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% Nd₂O₃ beads and around 0.5 wt% in the CeO₂
- beads. It is fair to assume that the uncertainty in CeO₂ and Nd₂O₃ 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 Nd/[Ce + Nd] ratio.
- 391 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 Nd/[Ce + Nd] ratio. According to Rudisill [37], Nd oxalate is slightly less soluble than Ce
- oxalate in 0.63 M nitric acid and 0.3 M excess oxalic acid ($45 \mu g/ml$ and $51 \mu g/ml$ 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
- lower solubility of Nd oxalate compared to Ce oxalate could have been a cc
 0.02 discrepancy in the expected and measured Nd/[Ce + Nd] ratio.
- 398 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
- 400 structures consistent with a $Ce_{1-x}Nd_xO_{2-(x/2)}$ structure and, hence, to permit the inference that the
- 401 Nd/[Ce + Nd] ratio corresponded to an x value.

402 **4.1.2 PXRD**

- 403 The PXRD patterns of the 900 °C calcined 25 °C and 60 °C oxalates are shown in Figure 3.
- 404 The literature indicated that CeO_2 and F-type $Ce_{1-x}Nd_xO_{2-(x/2)}$ (of low x) have Fm-3m structures (§
- 405 1.2.1) and that their PXRD patterns have similar peak positions, yet they shift relative to those of
- 406 CeO_2 (to lower 2 θ values) for the F-type solid solution with an increase in x value [19, 20]. Thus the
- 407 lattice parameter of the system should increase with an increase in x [19, 20]. C-type (Ia-3) Ce₁
- 408 $_xNd_xO_{2-{x/2}}$ oxides also have these peaks, and exhibit similar peak shift, but they have additional low
- 409 intensity peaks, as mentioned in § 3.1.
- 410 The PXRD patterns of the calcined 25 °C and 60 °C material had similar peak positions as shown in
- Figure 3. As the positions of the starred peaks were shifted relative to those of CeO_2 (to lower 20
- 412 values), there was no evidence of CeO_2 in either sample. This is illustrated in Figures 3b and 3c
- 413 where PDF 00-004-0593 corresponds to CeO_2 . The starred peaks had comparable positions to those
- of CeO_{1.53} (PDF 04-006-4613) and 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 conditionsprecluded it.
- 417 In addition to the main peaks (starred), low intensity peaks (not indicated by stars) were present in
- the PXRD patterns as shown in Figure 3a. Together, the main and low intensity were indicative of an
- 419 Ia-3 structured material. Figure 3b illustrates that the low intensity peaks had an improved signal-to-
- 420 noise ratio (achieved by using scan set b described in § 3.1) compared to those Figure 3a. The
- patterns showed no evidence of Ia-3 Nd_2O_3 (comparisons were made with PDF 04-015-1516 and PDF
- 422 04-004-8883) as shown in Figure 4a. However, the patterns had similar peak positions, yet shifted to
- lower 2θ values, to Ia-3 (C-type) Ce_{0.5}Nd_{0.5}O_{1.75} (stated as CeNdO_{3.5}, PDF 04-013-6624) as shown in
 Figure 4b. Thus, the PXRD data showed that each calcined 25 °C and 60 °C material was consistent
- with a C-type Ce_{1-x}Nd_xO_{2-(x/2)} solid solution. Finally, there was no evidence of A-type Nd₂O₃.
- 426 Gaussian curves were fitted using IDL (see the acknowledgements for further details) to the (2 2 2) 427 and (4 0 0) peaks of the PXRD patterns illustrated in Figure 3 to estimate their peak positions. These
- and (4 0 0) peaks of the PXRD patterns illustrated in Figure 3 to estimate their peak positions. These
 values were then used to provide first estimates of the lattice parameters of the calcined 25 °C and
- 429 60 °C oxalates. These particular peaks were chosen due to their large signal-to-noise ratios and
- 430 because they could be fitted more easily as they did not exhibit noticeable $K\alpha_{1,2}$ splitting. The
- 431 standard deviations of the fitted Gaussians were calculated from the estimated full widths at half
- 432 maxima to estimate the uncertainties in the peak positions and hence lattice parameters. The
- 433 averages of the lattice parameter estimates of the oxides made by the calcination of the 25 °C and
- 434 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. [19] (based on work by Bevan et al. [38]) that related the lattice parameter, a, of single phase (x < 0.73) Ce_{1-x}Nd_xO_{2-(x/2)} to x,

437
$$a = -5.366 (R_{iCe}(1-x) + R_{iNd}x)^2 + 12.10 (R_{iCe}(1-x) + R_{iNd}x) - 1.281,$$
 [1]

438 where $R_{i Ce}$ and $R_{i Nd}$ were the ionic radii of Ce and Nd, which were assumed to be 0.97 Å and 1.109 439 Å, respectively according to Horlait et al. [19]. This equation predicted that the lattice parameter of 440 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. 441 This was consistent with the lattice parameter estimates of the oxides in spite of their large 442 uncertainties.

443 4.1.3 Raman Spectroscopy

The varying blue line in Figure 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 ~590 cm⁻¹ (to 2 s.f.) but the ~530 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 ± 10 cm⁻¹ was assumed for all identified peaks, with the exception of ± 5 cm⁻¹ for the ~460 and ~590 cm⁻¹ peaks.

- 451 Horlait et al. [19] provided a literature review of past Raman spectroscopy analysis of CeO₂ and Ce₁.
- $xLn_xO_{2-(x/2)}$ solid solutions (Ln refers to lanthanides). The following discussion refers to some of its key
- 453 points as well as studies conducted by others.

- The literature indicated that CeO₂ [39, 40], F-type Ce_{1-x}Nd_xO_{2-(x/2)} [19] and C-type Ce_{1-x}Nd_xO_{2-(x/2)} [19] all have Raman peaks at around ~465 cm⁻¹. For example Cui et al. [39] observed this band in Raman spectra of CeO₂ 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 [19, 40]. The Raman band position for CeO₂ could also be affected by particle size [41, 42].
- 460 Regarding solid solutions, Horlait et al. [19] found the F_{2g} position to change from 461 cm⁻¹ to 453
- 461 cm^{-1} for CeO₂ through to Ce_{0.61}Nd_{0.39}O_{1.805}, and 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
- 463 wavenumber with increased Nd content from 466 cm⁻¹ to 452 cm⁻¹ for $Ce_{1-x}Nd_xO_{2-(x/2)}$ with x equal to
- 464 0.42 and 0.785, respectively (the latter showed evidence of additional A-type Nd₂O₃ being present
- too). Other Raman bands in the recorded spectrum needed to be inspected to ascertain if there was
- 466 evidence for a $Ce_{1-x}Nd_xO_{2-(x/2)}$ solid solution.
- 467 The Raman spectra of all calcined oxalates indicated the presence of a Ce Nd oxide solid solution by
- the ~590 cm⁻¹ band; McBride et al. [40], who used a Ar⁺ ion laser, found their Ce_{1-x}RE_xO_{2-y} materials
- 469 (including RE of Nd) to have a band near 570 cm⁻¹ in their Raman spectra. Dohčević-Mitrović et al.
- 470 [43], who used a 514.5 nm Ar⁺ laser, found peaks around 600 cm⁻¹ and 550 cm⁻¹ in their Raman
- 471 spectra of $Ce_{0.75}Nd_{0.25}O_{2-\delta}$ solid solutions, which they assigned to oxygen vacancies in their CeO_2 and 472 resulting from the solid solution mechanism, respectively. Horlait et al. [19] used a 633 nm laser and
- resulting from the solid solution mechanism, respectively. Horlait et al. [19] used a 633 nm laser and
 found the Raman spectra of their solid solutions to have peaks near 580 cm⁻¹, which they associated
- 474 with oxygen vacancies around metal ions for the A_{1g} and F_{2g} modes of M-O bonds. They found this
- 475 peak was always accompanied by a \sim 275 cm⁻¹ peak (the uncertainties in these values were not
- 476 reported). Thus the ~590 cm⁻¹ and ~260 cm⁻¹ peaks present in the spectra of the current study (Table
- 477 5) were consistent with a $Ce_{1-x}Nd_xO_{2-(x/2)}$ solid solution.
- 478 The peak at ~360 cm⁻¹ (see Table 5) in all spectra were indicative of an Ia-3 structure. Horlait et al.
- 479 [19] noted the presence of a 370 cm⁻¹ band and that although it is often associated with C-type (Ia-3)
- 480 Ln₂O₃, their XRD data suggested their material were solid solutions. They thus associated their 370
- 481 cm^{-1} with the C-type Ce_{1-x}Nd_xO_{2-(x/2)} structure. Similarly, the PXRD analysis in this study (§ 4.1.2)
- 482 negated the likelihood of C-type Nd_2O_3 . Thus the ~360 cm⁻¹ peak in each spectra was ascribed to the 483 presence of a C-type solid solution in each sample.
- A small potential peak at ~530 cm⁻¹ was also seen in the collected spectra as shown in Figure 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. [19]. The cause for this feature was unknown. The cause for the ~190 cm⁻¹ is yet to be assigned.
- 488 Ubaldini et al. [44] analysed C-type Nd₂O₃ 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.
- 490 between 425 and 450 cm⁻¹. However, Horlait et al. [19] associated a ~330 cm⁻¹ peak, as well as peaks
- 491 at ~430 cm⁻¹ ~480 cm⁻¹, with A-type Nd₂O₃. As there were no clear peaks at ~330 cm⁻¹ nor between
- 492 400 and 450 cm⁻¹, it was unlikely that Nd_2O_3 was present in either a C-type or A-type form. This
- 493 corroborated with the PXRD results in § 4.1.2.
- 494 The limited Raman spectroscopy studies of Am oxides have resulted in some uncertainties in the 495 collected $AmO_{2-(x/2)}$ ($Am_2O_{3+\delta}$) spectra [45, 46] and thus a comparison with the results in this study

- 496 were not made. Additionally it is noted that the Raman spectrometry data of Am oxide studies to 497 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-498 499 type $Ce_{1-x}Nd_xO_{2-(x/2)}$ and no evidence of Nd_2O_3 . However, PXRD was needed to negate the presence 500 of CeO₂.

4.2 The Effect of Oxalate Precipitation Temperature on Oxalate Particle Morphology 501 and Size Distribution 502

503 4.2.1 Scanning Electron Microscopy

504 Figure 6 illustrates examples of ESEM images taken of 25 °C oxalate precipitates. The particles were 505 lath shaped and had a large range of sizes. Qualitatively, the 60 °C oxalate particles were larger than the 25 °C precipitates. The SEM analysis also showed evidence of lath shaped 60 °C oxalate particles. 506 507 The 60 °C samples exhibited charging.

508 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 509 510 crumbled easily into a fine powder with a similar consistency to common talc. It is highlighted that

511 these respective macroscopic behaviours were also exhibited by their oxides.

512 **Particle Size Analysis** 4.2.2

513 For brevity, the particle size distributions of the 60 °C and 25 °C precipitated oxalates determined 514 using only two of the optical models are illustrated: the Ce Oxalate Max and UO_2 (see Figure 7). The

515 mode values are indicated by the positions of the maximum intensity peaks of each distribution.

516 The exact values of the particle size distributions depicted in Figure 7 are only an approximation of 517 the PSDs due to the assumptions used to process the data, namely, the refractive indices and that 518 the particles were spherical. The trends of the particle size distributions give a general indication of 519 what would be expected under the sample production conditions used. The analytical method could

520 only be used for the purposes of determining whether the precipitation conditions generated

521 relatively distinct particle size distributions, owing to the assumptions used.

522 Table 4 shows that the median particle sizes (d_{50}) of the 25 °C Ce Nd oxalates were smaller than 523 those of 60 °C Ce Nd oxalates by around 10 μ m. Figure 7 shows there were two distinct sets of PSDs

524 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

525 526 material had a smaller modal particle size than the 60 °C oxalate, but all batches contained particles

527 covering a wide size range. These conclusions were corroborated by the ESEM observations noted in

528 § 4.2.1. The optical model choice was sometimes found to affect the PSD shape for a given sample

529 e.g. by affecting the number of peaks. This can be seen by comparing Figure 7a and 7b, particularly

530 for the 60 °C oxalate material. Nonetheless, this did not affect the observation that the particle size

531 distributions of the 25 °C and 60 °C oxalate precipitates were resolvable with respect to

532 temperature regardless of the optical model used.

533 The production method was able to create material with different median and modal particle sizes 534 without the need for ball-milling but respirable fines (sub 10-µm particles) were created using both

- precipitation temperatures as shown in Figure 7. Claparède et al. [12] found that Ce oxalate
- agglomerates shrank in size by around 25 % on conversion to CeO_2 . It is thus assumed that on
- 537 conversion, the Ce Nd oxalate particles of this study would shrink. Thus more respirable fines could
- 538 be produced.

539 5 Concluding Remarks

540 The ESA programme has identified the potential need to conduct sintering studies with $AmO_{2-(x/2)}$ 541 species for 0.5 < x < 0.7. However investigations with surrogate oxides are an effective precursor 542 providing some initial insight prior to carrying out specific tests with Am oxides. A hypothesis was 543 that $Ce_{1-x}Nd_xO_{2-(x/2)}$ could be used as a mixed metal oxide surrogate for certain $AmO_{2-(x/2)}$ species and 544 that different oxygen to metal ratios (O/M) could be targeted by changing the molar ratio of the metal nitrate feeds as the latter had been possible in a study by Higashi et al. [27]. The theory 545 546 suggested that only the ratio of the metals in the oxide i.e. Nd/[Ce+Nd], needed to be measured to 547 determine x and hence the O/M ratio.

- 548 This study has demonstrated a production route for creating $Ce_{1-x}Nd_xO_{2-(x/2)}$ with a nominal target of
- 549 x equal to 0.60. A number of analysis procedures have been used and developed to characterise

550 oxide composition and structure as well as oxalate particle characteristics. The oxalate precipitation 551 method enables material to be created continuously with minimal attendance, which would be an

552 advantage for regular production.

- 553 Oxalate precipitates were created under a range of conditions to investigate the impact of changing
- the precipitation mixing rate and 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 Nd/[Ce+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
- 558 being able to produce a reproducible material as reproducible surrogates would be essential for
- 559 sintering trials. The results also demonstrated that the ratio was precipitation temperature
- 560 independent.
- 561 Powder X-ray diffraction and Raman spectroscopy analyses showed that the production process
- 562 created $Ce_{1-x}Nd_xO_{2-(x/2)}$ with Ia-3 structure without additional Nd_2O_3 . Although the O/M ratio was not 563 measured directly, the fact that the oxides had structures consistent $Ce_{1-x}Nd_xO_{2-(x/2)}$ suggested that x
- values of 0.62 had been achieved i.e. $Ce_{0.38}Nd_{0.62}O_{1.69}$ had been made. However, the small
- 565 discrepancy of around 0.02 showed that an x-value can be affected by experimental processes
- 566 (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 better constrain the lattice parameter
- 568 estimate.
- 569 The literature review has highlighted that more experimental Am oxide crystallographic data is
- 570 needed to create a more detailed Am-O phase diagram with greater certainty. This is particularly
- 571 important to the ESA programme for Am oxide sintering studies. From a surrogate stand point, the
- 572 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
- 574 experimental studies are needed for species near AmO_{1.69}. Additionally, high temperature
- 575 crystallographic data of $Ce_{0.38}Nd_{0.62}O_{1.69}$ would be needed too. Once these data are obtained then
- the suitability of $Ce_{0.38}Nd_{0.62}O_{1.69}$ as a crystallographic surrogate can be assessed. However, the indications suggest it is a potential surrogate based on the room temperature knowledge of

- 578 Ce_{0.38}Nd_{0.62}O_{1.69} and limited data about oxides near AmO_{1.69}, particularly as the C' (Ia-3) phase has a
- tentative phase boundary in the Am-O phase diagram by Thiriet et al. [9] (see Figure 1). Future work
- should also include high temperature XRD investigations with $Ce_{1-x}Nd_xO_{2-(x/2)}$ to develop a phase
- 581 diagram such that other $Ce_{1-x}Nd_xO_{2-(x/2)}$ phases can be assessed for surrogate suitability at high
- 582 temperature.
- 583 It has been shown that $Ce_{1-x}Nd_xO_{2-(x/2)}$ with a target x value can be made easily to within some
- uncertainty and thus there is the potentially to create $Ce_{1-x}Nd_xO_{2-(x/2)}$ with different x values readily,
- if needed. Although the focus is on higher x values, the literature indicates that $Ce_{1-x}Nd_xO_{2-(x/2)}$
- system up to x equal to around 0.4 is FCC in structure. Thus, there is also the potential to create and
 use it as a surrogate for FCC AmO_{2-(x/2)} up to around x equal to 0.4, should this range ever be
- 588 considered.
- 589 This study has shown that the oxalate precipitation temperature can have a noticeable impact on 590 oxalate particle size: those precipitated at 60 °C (at 250RPM) were larger by around 10 μm (median
- 591 particle size) than the lath shaped particles precipitated at 25 °C (at 250 RPM).
- 592 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
- 594 made to ensure that respirable particles do not become airborne to minimise the possibility of
- 595 damage to personnel health.
- 596 Oxide particle size could impact how well materials sinter into discs or pellets, and potentially
- 597 influence sintered body integrity and mechanical properties. The ability to sinter an integral pellet
- 598 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
- 601 MO_{2-X} form with a range of sizes. Thus if the solid solution is a suitable surrogate, small scale 602 sintering trials should be conducted with $Ce_{1-x}Nd_xO_{2-(x/2)}$ powders made from 25 °C and 60 °C (250
- 602 sintering trials should be conducted with Ce_{1-x}N
 603 RPM stirring rate) oxalates.

604 6 Appendix A: PXRD and Raman Spectroscopy Analysis of Oxalates

605 **6.1 PXRD**

Early trials of oxalate material were made using a similar method outlined at the start of § 2.1.

- 607 Differences included a shorter precipitation duration and using a 150 RPM stirring rate with a 25 °C
- 608 precipitation temperature. The material was consistently a pink-lilac colour. To confirm that the
- 609 precipitation procedure was producing oxalates, one of these early samples underwent PXRD. The
- 610 diffraction pattern was collected from 4 $^{\circ}$ to 90 $^{\circ}$ using a 0.5 s step time and a 0.01 $^{\circ}$ 20 step size. The
- data were collected from 4° to 90° using a 0.5 s step time and a 0.01° 2θ step size. The PXRD
- 612 pattern is illustrated in Figure A.1 for the 2θ angular range of 5 ° to 60 °. The pattern is consistent
- 613 with those of monoclinic (P21/c) rare earth oxalate hydrates, such as cerium (III) oxalate hydrate
- 614 (PDF 00-020-0268) and neodymium (III) oxalate hydrate (PDF 00-020-0764).
- All future samples made (according to the conditions noted in Table 3) were similar in colour to this
- 616 early trial material analysed by PXRD. It was assumed that all precipitated samples were similar
- 617 oxalates. Raman spectroscopy was used to analyse these future samples in order to validate the
- 618 assumption.

619 6.2 Raman Spectroscopy

- An example of a Raman spectrum taken of a single location in a 60 °C oxalate precipitate (see Table
- 621 3) is shown in Figure A.2. The spectrum is similar and comparable with that of
- 622 $Ce_{0.715}Nd_{0.285}(C_2O_4)_{1.5}$, 5H₂O presented by Horlait et al. [19] in their supporting information. The
- 623 wavenumber range of 200 to 1800 cm⁻¹ is shown in Figure A.2 to aid this comparison. The Raman
- 624 spectra of the precipitates were thus consistent with Ce Nd (III) oxalate.

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- 631 oxides, T. Knott who provided advice for XRF calibration uncertainty estimates, and D. Vernon and T.
- 632 Crawford who supported the set-up and maintenance of the pumps are gratefully acknowledged.

633 8 Figures and Tables.

Table 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.

Am oxide	Symmetry	Space Group	Lattice Parameters (only lengths) (Å)	Surrogate	Symmetry	Space Group	Lattice Parameters (only lengths) (Å)
AmO ₂	Face centred cubic (fluorite- type) [9] [47]	Fm-3m [47] *	5.374 [48]	CeO ₂ [19]	Face centred cubic (fluorite- type) [19]	Fm-3m [19]	5.41134(8) [19]
A- Am ₂ O ₃	Hexagonal [49] Hexagonal	P-3m1 [49] P6 ₃ /mmc	a ₀ =3.817 c ₀ =5.971 [49]	A-Nd ₂ O ₃	Hexagonal [19] Hexagonal	P-3m1 [19] ⁺ P6 ₃ /mmc	a ₀ =3.83120 c ₀ =6.00170 PDF 01-079- 9858
	[24]	[24]			[50]	[50]	
B- Am ₂ O ₃	Monoclinic [48]	C2/m [48] ^Δ	a ₀ =14.38 b ₀ =3.52 c ₀ =8.92 [48]				

C-	Body	la-3 [24] †	11.03 [48]	$C-Nd_2O_3$	Body	la-3 [52]	11.1 [52]
Am_2O_3	centred				centred	[53]	
	cubic [48]				cubic [52]		

636 * + Unit cell illustrations can be found in Figure 8.9 (p. 1358) by Runde et al. [48].

637 + Δ Unit cell illustrations of the (rare earth) surrogate oxides can be found in Figure 3.16 (p. 74) by

638 Schweda et al. [51]. It is noted that Chikalla et al. [25] suggested that B-type Am2O3 was likely to have the

639 same structure as a B-type rare earth sesquioxide.

640

641Table 2: approximate x-ranges for $Ce^{IV}_{1-x}Nd^{III}_{x}O_{2-(x/2)}$ according to Horlait et al. [19]. Note the exact solubility642limits are not stated as only discrete x values were investigated.

Structure	x value
F-type	x ≤0.39
C-type	0.42 ≤ x < 0.73
C -type and A -type Nd_2O_3	x > 0.73

643

644 Table 3: the oxalate precipitation experimental matrix.

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

645

646 Table 4: mean d₅₀ values of the suspended Ce Nd Oxalate precipitate vials determined using different

647 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

649	Table 5: The estimated peak positions of oxide sample spectra that were reasonably well fitted. N/A	
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650 signifies that it was not fitted. Conservative uncertainties of $\pm 10 \text{ cm}^{-1}$ are assumed for all peaks except ~459 651 and ~590 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

652



- Figure 1: The tentative Am-O phase diagram1 by Thiriet et al. [9], which also illustrates data (circles)
- measured by Sari et al. [17]. The C phase corresponds to cubic (Ia-3) Am₂O₃; the A phase to hexagonal

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 Am_2O_3 ; the C' phase to a higher temperature cubic (Ia-3) phase and all α phases to face centred cubic AmO_2 .

657 _(x/2).



658

659 Figure 2: A schematic of the oxalate precipitation apparatus.



Figure 3: Powder X-ray diffraction patterns of the first 900 °C calcined 25 °C (blue) and 60 °C oxalate (red)
 precipitates (see Table 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 CeO₂. 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. PDF cards are illustrated. Their intensities have been increased to aid comparisons of peakpositions only.



Figure 4: Powder X-ray diffraction patterns of the first 900 °C calcined 25 °C (blue) and 60 °C oxalate (red)
precipitates (see Table 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 2θ, 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



673 Ce1-xNdxO2-(x/2) solid solutions. The calcined 60 °C oxalate XRD patterns have been offset vertically to 674 improve clarity. The intensities of the PDF cards were increased to aid comparisons of peak positions only.

675

676 Figure 5: The varying blue line is a background removed and normalised Raman spectrum of the second calcined 25 °C oxalate precipitate (see Table 3). The spectrum is illustrated between 100 and 750 cm⁻¹. It 677 678 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 deconvolved 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. 679

680



683 684 Figure 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.

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Figure 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 represented with one colour/symbol and similarly for the 60 °C oxalates, to aid the comparison between the

692 25 °C and 60 °C oxalates.



Figure A.1: PXRD pattern of the precipitated material made using similar conditions (25 °C, 150 RPM) to those outlined in Table 3. The angular range from 5 ° to 60 ° is illustrated.



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694

- Figure A.2: Raman spectrum of the first 60 °C oxalate sample (made using condition C). Only the
 wavenumber range from 100 to 1800 cm⁻¹ is illustrated to aid comparison with the study by Horlait et al.
- 700 [19].

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