

Detailed X-ray Diffraction Analysis of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ as a Surrogate for Substoichiometric Americium Oxide

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Abstract

European Space Agency (ESA) radioisotope power systems will use ²⁴¹Am as their heat source. The chemical form of the americium oxide has yet to be decided but an option that may be investigated in future research are certain Ia-3 $\text{AmO}_{2-(x/2)}$ phases. In a previous investigation, Ia-3 (C-type) $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with x values between 0.5 and 0.7 were proposed as candidate surrogates (Watkinson et al., 2017). A continuous oxalate precipitation and calcination route for fabricating such oxides was presented and the means to target an x value was described (Watkinson et al., 2017). An initial estimate of the lattice parameter was provided in the previous study by fitting Gaussians to X-ray diffraction data peaks. Previous quantitative X-ray fluorescence analysis suggested an x-value of 0.61 had been achieved. Characterising the crystal structure and the oxygen-to-metal ratio, which corresponds to x, of an oxide powder will be essential data for future sintering studies where changes in these parameters will be investigated.

In this study, a Rietveld refinement investigation is presented, which has enabled the lattice parameter of the material to be better constrained and estimated more precisely. The result is consistent with the literature; a lattice parameter-x value relationship in the literature was used to estimate the x value using this improved estimate and it confirmed an x value of 0.6 has been made. This investigation has thus further validated the previously presented synthesis method and characterised the crystal structure of the material more precisely in preparation for future sintering trials.

1 Introduction

The European Space Agency (ESA) is funding a research and development programme into making americium fuelled radioisotope power systems (RPSs) to provide electrical and thermal power to spacecraft in extreme environments, such as deep space and planetary surfaces. A range of technologies, including radioisotope thermoelectric generators, Stirling generators and heater units, are being developed [1, 2].

The research and development of the americium-241 oxide fuel form is an essential part of the ESA programme. Investigations into how to process and sinter ²⁴¹Am oxide powders into pellets are being carried out e.g. as presented in the paper by Sarsfield et al. [3]. Fundamental to this area of research, is the development and sintering trials of a variety of surrogates for a range of americium oxides [4, 5]. For example, a variety of sintering investigations with CeO_2 and Nd_2O_3 have been conducted to infer how AmO_2 and Am_2O_3 may behave during sintering under different conditions [6]. Understanding how the crystalline structure of surrogates vary under a variety of sintering conditions is essential to developing the fuel form for americium oxide based RPSs. For example, volume changes associated with crystallographic phase changes may impact the ability to sinter the powder into intact

44 pellets [4]. The characterisation of the oxide powders prior to their sintering is thus essential to these
45 studies.

46 One of the americium oxides of interest to the ESA programme is a substoichiometric form, namely,
47 Ia-3 $\text{AmO}_{2-(x/2)}$. In a previous study, Ia-3 (C-type) $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ with x values between 0.5 and 0.7 were
48 proposed as candidate surrogates for certain Ia-3 $\text{AmO}_{2-(x/2)}$ [4]. A synthesis method where Ce Nd
49 oxalates were continuously co-precipitated from the reaction of Ce and Nd nitrate and oxalate feeds
50 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
51 mixing the metal nitrates in an appropriate corresponding molar ratio [4]. Powder X-ray diffraction
52 (PXRD) and Raman spectroscopy analyses confirmed the synthesis of Ia-3 $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ material [4].
53 Additionally, quantitative X-ray fluorescence (QXRF) established that each material was made with a
54 reproducible Nd/[Ce+Nd] ratio of 0.62 with a coefficient of variation of around 0.1 % [4] and its
55 uncertainty was estimated to be ± 0.01 . It has since been noticed that a slight numerical oversight was
56 made in the previous paper [4]. The x value should have been stated as 0.61 with a coefficient of
57 variation of around 0.1 % and an estimated uncertainty of ± 0.01 . Thus the QXRF analysis confirmed
58 that this co-precipitation method can be used to target an x value for a Ce Nd based oxide solid
59 solution.

60 The volume of the unit cell of a solid solution phase can often be related to the molar composition
61 (fraction) of a dopant species e.g. x, by some function. In the case of cubic systems, this would thus
62 correspond to a relationship between the unit cell parameter and the x value. Assuming the
63 relationship is known for a given solid solution system, then the molar composition of a given phase
64 can be inferred by using an experimentally determined lattice parameter. In the case of $\text{AmO}_{2-(x/2)}$
65 species and their surrogates, this means that an estimate of the oxygen-to-metal ratio can be
66 determined. It therefore should provide an alternative method to QXRF for the Ce Nd mixed oxide
67 surrogates. Epifano et al. (2017) have recently published the relationship between lattice parameter
68 and oxygen-to-metal ratio for AmO_{2-x} as a function of X for values 0 and 0.4 (note this is an alternative
69 notation where X equals x/2) and temperature [7]. Vauchy et al. (2016) and Vauchy et al. (2015), who
70 studied hypostoichiometric uranium-plutonium-amerium mixed oxides and hypostoichiometric
71 uranium-plutonium mixed oxides, respectively, noted that the use of a lattice parameter
72 determination to estimate the oxygen-to-metal ratio of an oxide provides an estimate based on the
73 oxide's surface owing to the limited penetration depth of the X-rays [8, 9]. They highlighted that
74 thermogravimetric analysis provides an estimate of the oxygen-to-metal ratio of the bulk material [8].

75 The relationship developed by Horlait et al. [10] for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system up to x equal to 0.73
76 relates the lattice parameter, a , and x by a quadratic equation, namely,

$$77 \quad a = -5.366 (R_{i\text{Ce}}(1-x) + R_{i\text{Nd}}x)^2 + 12.10 (R_{i\text{Ce}}(1-x) + R_{i\text{Nd}}x) - 1.281. \quad (1)$$

78 The $R_{i\text{Ce}}$ and $R_{i\text{Nd}}$ terms refer to the Ce and Nd ionic radii, respectively, and were assumed to be equal
79 to 0.97 Å and 1.109 Å, respectively [10]. The solid solution is known to undergo a phase transition
80 from an Fm-3m cubic phase (commonly referred to as F-type) to the superstructure Ia-3 cubic phase
81 (commonly referred to as C-type) at around x equal to 0.42. This transition to the Ia-3 form requires
82 it to have a lattice parameter that is twice as large as the Fm-3m form. However, as the x value
83 proceeds to increase, the lattice parameter continues to expand. In order to compare the lattice
84 parameter variation of the system with an increase in x, Horlait et al. [10] halved all lattice parameters
85 for the Ia-3 phases.

86 In the previous study by Watkinson et al. [4], an initial estimate of the lattice parameter of the
87 synthesised Ia-3 $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ (with a 0.62 Nd/[Ce+Nd] ratio) was determined to be 5.51 Å +/- 0.01
88 Å (Note that this estimate did not rely on the value of the ratio and is thus unaffected by the ratio
89 being corrected to 0.61.). This was calculated from the 2θ positions of specific diffraction peaks, which

90 were determined by fitting Gaussian profiles to them. Additionally, Equation 1 was used to predict
91 the half-value lattice parameter that would be expected for a $Ce_{1-x}Nd_xO_{2-(x/2)}$ phase with an x value of
92 0.62. This was confirmed to be 5.51 Å to 3 s.f. For completeness, the lattice parameter for a $Ce_{1-x}Nd_xO_{2-$
93 $(x/2)$ phase with the corrected x value of 0.61 has been calculated: 5.51 Å to 3 s.f. The predicted lattice
94 parameter was thus consistent with the estimate made by the aforementioned peak position
95 procedure.

96 The objective of this presented study was to focus on a powder X-ray diffraction investigation using
97 Rietveld refinement to determine the lattice parameter of the $Ce_{1-x}Nd_xO_{2-(x/2)}$ material more precisely
98 than was previously achieved by Watkinson et al. using the aforesaid simple diffraction peak position
99 analysis method [4]. Unlike the peak position method, Rietveld refinement would allow other factors
100 that impact peak position to be accounted for e.g. the effect of the instrument contribution to the
101 diffraction data. This refinement will:

- 102 1) Be useful for future surrogate sintering studies as part of the ESA space nuclear power
103 programme where the impact of the sintering conditions on crystallography, specifically to
104 cause phase changes or changes in the lattice parameter, will need to be characterised as
105 these will be related to volume changes in the fuel, which could impact sintering. In addition
106 to this, it will also be important to establish any changes in the O/M of the surrogate materials
107 caused by different sintering conditions. Establishing the lattice parameter of the surrogate
108 materials before and after sintering conditions is therefore of interest for both purposes.
- 109 2) Allow a more precise inference of the x value (using Equation 1) from diffraction data to
110 establish if it was consistent with the QXRF (0.61) value of the previous study, as well as the
111 literature.

112 2 Method

113 A cerium neodymium oxide was synthesised by an oxalate co-precipitation and calcination route using
114 the method outlined by Watkinson et al. [4] (the precipitation temperature was 25 °C and the
115 calcination temperature was 900 °C). It was thus assumed to have an Nd/[Ce+ Nd] ratio, and thus an
116 inferred x value, of 0.61(1). An agate pestle and mortar was used to process the Ce Nd oxide material
117 into a powder for powder X-ray diffraction analysis. Previous scanning electron microscopy analysis
118 of oxalate material made using this route found it to be composed of lath-shaped particles [4]. The
119 literature suggests that the morphology is conserved on calcination to the oxide [10]. It was suspected
120 that this morphology could cause preferred orientation effects (texture) in the oxide powder X-ray
121 diffraction data. The powdered sample was sprinkled onto an off-cut silicon single-crystal. This acted
122 to reduce both the background holder contribution, and potential preferred orientation.

123 A Bruker D8 Advance Powder Diffractometer (with a LynxEye Position Sensitive Detector) was used to
124 acquire the powder X-ray diffraction data using copper $K_{\alpha 1}$ radiation in a Bragg-Brentano θ - θ
125 configuration. Data were acquired over a 20-150° 2 θ -range using a step size of 0.011° 2 θ and a total
126 counting time of 28 hours.

127 The MAUD (Materials Analysis Using Diffraction) programme was used to Rietveld refine the
128 diffraction data [11]. The NIST LaB6 SRM660b standard powder was used to refine the instrumental
129 contribution (peak width evolution with 2 θ , peak shapes and Gaussian-Lorentzian components, z-
130 displacement parameter). A Crystallography Open Database (COD) [12] file, namely, COD 1548619,
131 for Ia-3 $Ce_{0.5}Nd_{0.5}O_{1.75}$ by Chakraborty et al. [13] was used as the starting phase file. Although their
132 diffraction data were recorded using a neutron source, it provided an initial starting point for the
133 analysis by providing nominal values for the cell parameter, occupancy, fractional atomic positions
134 (x,y,z) and isotropic atomic displacement parameters (B_{iso}) of the analysis.

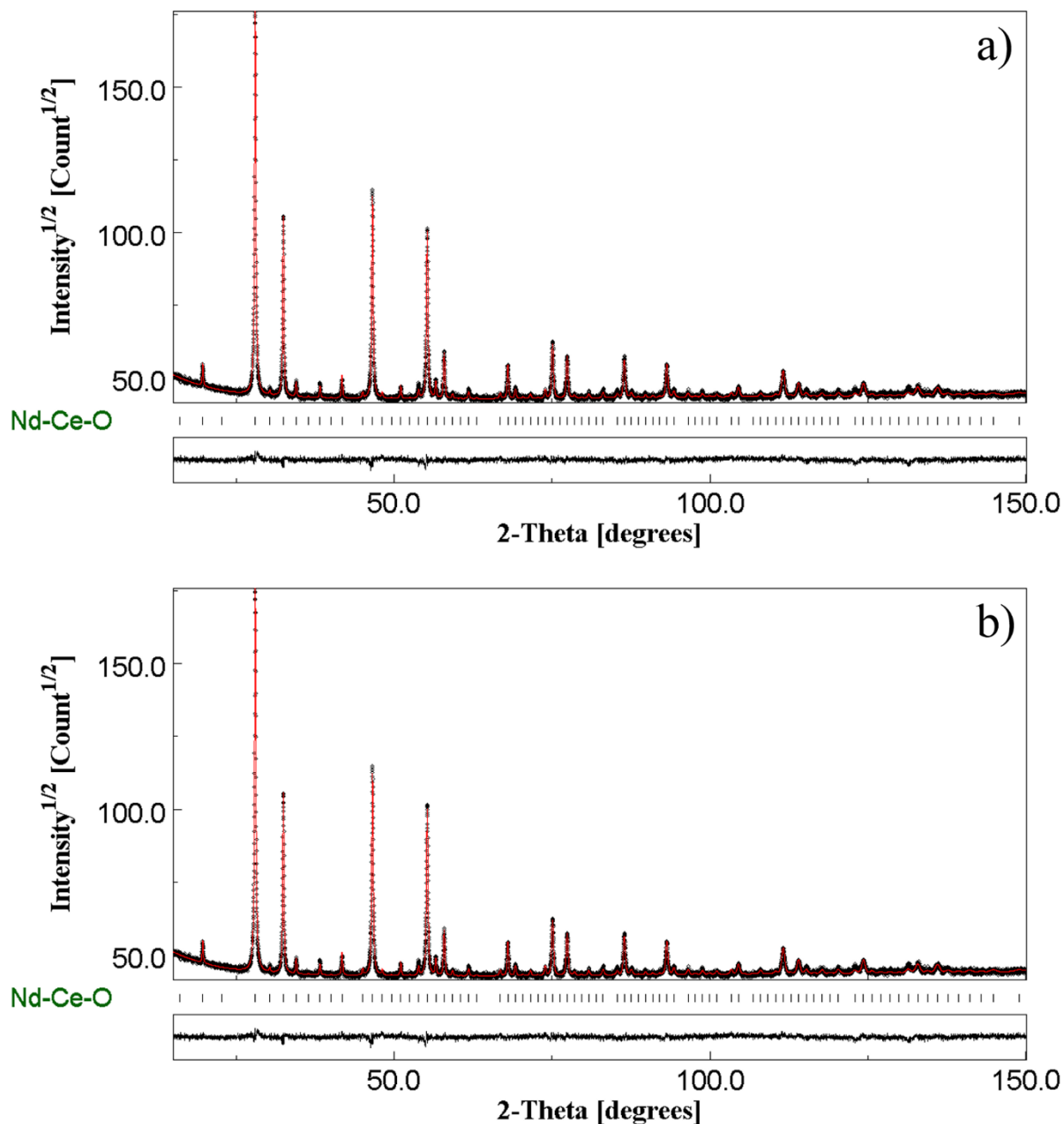
135 The zeroth order background term and overall scale factor were initially visually estimated. The
136 background was then modelled using a 4th degree polynomial. Further increase of the polynomial
137 order did not improve the refinement. The analysis first proceeded with the refinement of the
138 intensity scale and unit cell parameter, followed by the 2 θ offset. The isotropic crystallite size
139 parameter was refined and a default microstrain value of 6×10^{-4} was assumed. In an attempt to
140 establish the impact of an anisotropic mean size on the refinement, the Popa model [14] was
141 employed where the zeroth (isotropic) and then the first order parameters were refined. This was
142 followed by the zeroth and first order microstrain terms for the Popa model [14]. The reader is
143 referred to an introductory overview of the Popa model [15]. As Ce and Nd ions have similar atomic
144 numbers, it was unlikely that the X-ray diffraction data would be able to refine the occupancies of the
145 Nd and Ce ions. The occupancies of the Ce and Nd ions were fixed according to the Nd/[Ce+Nd] ratio
146 of 0.61 (see the bottom half of Table 2). The refined structural parameters of Ce_{0.5}Nd_{0.5}O_{1.75} by
147 Chakraborty et al. [13] were consulted to identify the fractional atomic positions that were permitted
148 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
149 of Table 2. As X-rays are less sensitive in the determination of B_{iso} parameters than neutrons, the B_{iso}
150 values of all atoms were assumed to be the same as Chakraborty et al. [13] who refined neutron
151 diffraction data.

152 The isotropic atomic displacement parameters (B_{iso}) of the cations were then considered. Two
153 approaches were taken: 1) to use a single general B_{iso} parameter for all cations where the parameter
154 for one atom was refined (Ce1) and 2) to refine the results using the B_{iso} values presented by
155 Chakraborty et al. [13] as fixed values. In both cases, the B_{iso} values of the oxygen atoms were equated
156 to that of Chakraborty et al. [13]. The occupancies for the oxygen atoms were then refined for each
157 case. It was decided that as the Ce2 and Nd2 atoms should have the same fractional coordinates,
158 these were then refined only for the Ce2 atom sites where those of the Nd2 atoms were set to have
159 values equal to these. The results were then compared for both approaches.

160 **3 Results**

161 Figure 1 illustrates the recorded and the refined PXRD patterns of the analysed Ce_{1-x}Nd_xO_{2-(x/2)} material
162 using the two approaches for isotropic atomic displacement parameters (B_{iso}) of the cations. The
163 refined cell and structural parameters are outlined in Table 1 and Table 2, respectively. The bond
164 distances between the cations and anions for each model are shown in Table 3. The half-value of the
165 refined lattice parameters were both thus 5.51101(4) Å. The relationship between the lattice
166 parameter and the x value for Ce_{1-x}Nd_xO_{2-(x/2)} system (for x values up to 0.73) that was developed by
167 Horlait et al. [10], namely, Equation 1, is shown in Figure 2. The figure also illustrates their
168 experimental data [10]. The half-value of the lattice parameters refined in this study are plotted as a
169 single point in each of Figures 2a and 2b where the x value was assumed to be 0.61(1) according to
170 Watkinson et al. [4], for the purpose of plotting. Additionally, the quadratic Equation 1 was solved for
171 x using the half-value of the refined lattice parameters, namely, 5.51101(4), to provide a more precise
172 estimate of the x value of the Ce_{1-x}Nd_xO_{2-(x/2)} material. The solution was an x value of 0.602 (when the
173 uncertainties in *a* were considered the uncertainty in x was + 0.001/- 0.000 to 3.s.f).

174 As was stated in the Introduction, the lattice parameter of a Ce_{1-x}Nd_xO_{2-(x/2)} phase with the corrected
175 x value of 0.61 was predicted using Equation 1 to be: 5.51 Å to 3 s.f. The result was consistent with
176 the lattice parameter estimates from peak position estimates determined by Gaussian curve fits to
177 diffraction peaks [4]. As this Rietveld refinement study has enabled the lattice parameter to be
178 determined more precisely, the predicted value is stated to a greater number of significant figures i.e.
179 5.512(1) Å to 4 s.f. for comparison. This states the uncertainty in the predicted lattice parameter
180 associated with the estimated uncertainty in the assumed QXRF value.



181

182 Figure 1: Illustrates the experimental PXRD pattern for the synthesised $Ia-3$ $Ce_{1-x}Nd_xO_{2-(x/2)}$ (black circles); the
 183 Rietveld refined pattern (red line) and the residuals of the fit a) when a general B_{iso} parameter was refined for
 184 the cations and b) when the cation B_{iso} values of Chakraborty et al. [13] were used.

185 Table 1: The refined parameters and associated data. The values in brackets are the estimated standard
 186 deviations (based on 1σ of a normal distribution) associated with the fitting procedure.

Refinement of General B_{iso} for all Cations	
Parameter/Refinement Data	Value
Lattice Parameter, a (Å)	11.02201(9)
2θ offset (°)	-0.0041(3)

Average crystallite size (Å)	462(1)
Microstrain	6.33(6) x 10 ⁻⁴
R _{wp} (%)	2.40
R _{exp} (%)	2.19
Goodness of Fit	1.09

Fixed Chakraborty et al. [13]. cation B_{iso} values.

Parameter/Refinement Data	Value
Lattice Parameter, <i>a</i> (Å)	11.02202(8)
2θ offset (°)	-0.0041(3)
Average crystallite size (Å)	464(1)
Microstrain	6.50(6) x 10 ⁻⁴
R _{wp} (%)	2.39
R _{exp} (%)	2.19
Goodness of Fit	1.09

187

188 *Table 2: The refined structural atomic parameters of Chakraborty et al. [13] are stated in the top half of the*
189 *table and the structural parameters of this study are provided in the bottom half of the table. * Fixed according*
190 *to QXRF assumption from the previous study, namely, an assumed x value of 0.61 [4]. The values have been*
191 *presented using the same notation as Chakraborty et al. [13] for consistency.*

Atom	Site	X	Y	Z	B _{iso} (Å ²)	Occupancy
<i>Chakraborty et al. [13].</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)

This study. Results with a general isotropic displacement parameter for cations.

Nd1	8b	0.250	0.250	0.250	1.12(1)	0.102*
Ce1	8b	0.250	0.250	0.250	1.12(1)	0.065*
Nd2	24d	-0.01772(9)	0	0.250	1.12(1)	0.305*
Ce2	24d	-0.01772(9)	0	0.250	1.12(1)	0.195*
O1	48e	0.389(1)	0.139(1)	0.376(2)	1.305	0.852(7)
O2	16c	0.403(2)	0.403(2)	0.403(2)	2.431	0.170(6)

This study. Results that used Chakraborty's isotropic displacement parameter for cations [13].

Nd1	8b	0.250	0.250	0.250	1.293	0.102*
Ce1	8b	0.250	0.250	0.250	1.293	0.065*
Nd2	24d	-0.01800(7)	0	0.250	0.893	0.305*
Ce2	24d	-0.01800(7)	0	0.250	0.893	0.195*
O1	48e	0.388(1)	0.140(1)	0.378(2)	1.305	0.834(7)
O2	16c	0.393(2)	0.393(2)	0.393(2)	2.431	0.157(6)

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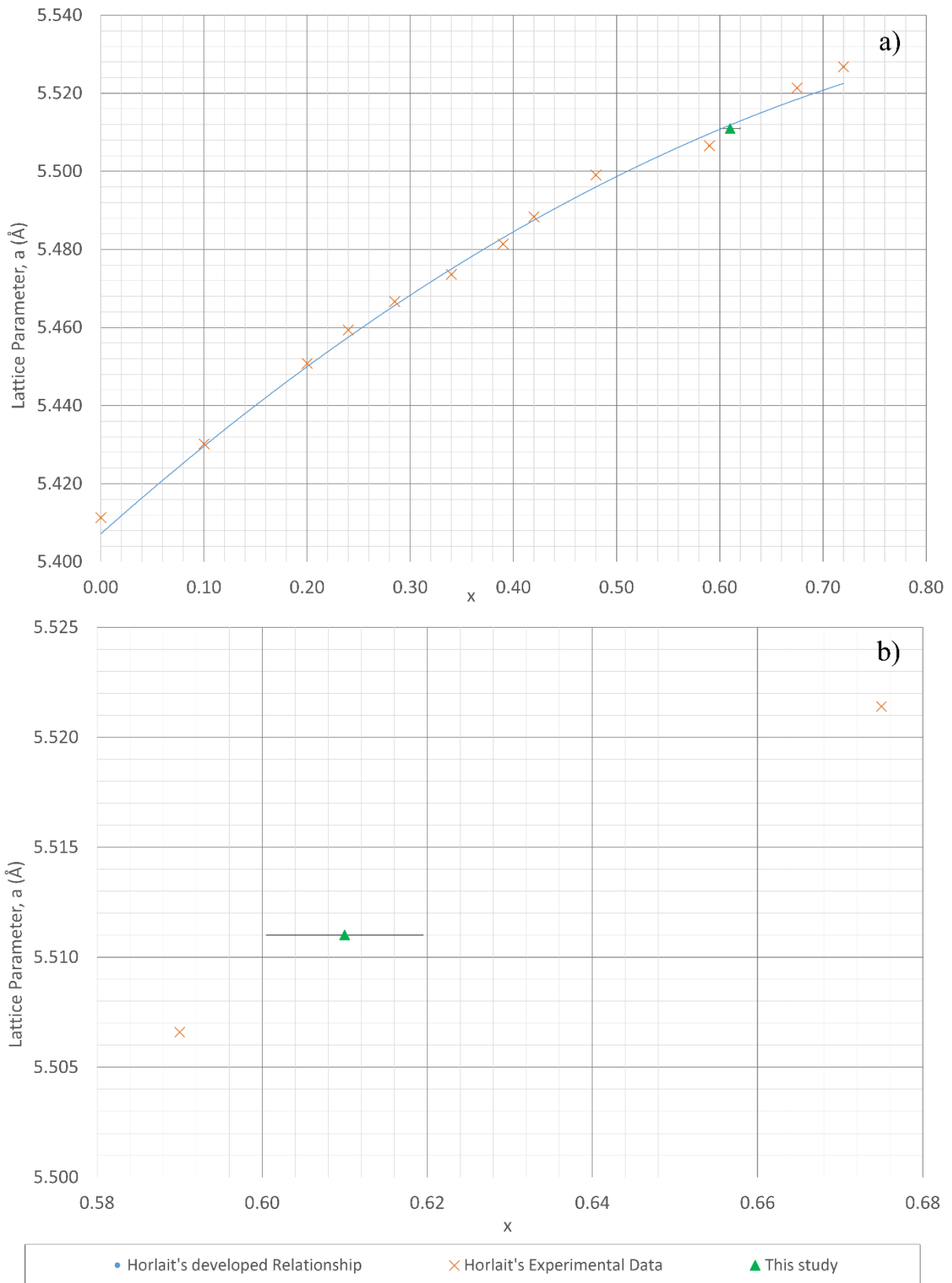
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Table 3: The Atomic bond distances of the results refined for each model.

Atomic Site	Atomic Site	Atomic Bond Distance (Å)	
		<i>Refinement with a general isotropic displacement parameter for cations.</i>	<i>Refinement that used Chakraborty's isotropic displacement parameter for cations [13].</i>
Ce1	O1	2.40	2.40
Ce1	O2	2.93	2.73
Nd1	O1	2.40	2.40
Nd1	O2	2.93	2.73
Ce2	O1	2.31	2.32

Ce2	O2	2.36	2.40
Nd2	O1	2.31	2.32
Nd2	O2	2.36	2.40

194



195

196 *Figure 2: Illustrates the lattice parameter- x relationship developed by Horlait et al. [10] for the $Ce_{1-x}Nd_xO_{2-(x/2)}$*
 197 *system (solid blue line) with their experimental (red cross) data illustrated. The lattice parameter (triangle)*
 198 *determined for the oxide synthesised in this study is consistent with the data. The material is assumed to have*
 199 *an x value and uncertainty of 0.61(1) [4]. a) Illustrates the data over the entire x -range over which the Horlait*
 200 *et al. [10] relationship is valid and b) over x values near 0.61.*

201 4 Discussion

202 In this study a Ce Nd oxide made using the process described by Watkinson et al. [4] has undergone
203 PXRD analysis using two slightly different approaches. The refined lattice parameters were found to
204 be very similar to each other as shown in Table 1. The R_{wp} and Goodness of Fit parameters (see Table
205 1) together with the residuals (see Figure 1) indicate that good fits were achieved in both cases.

206 It was previously observed that oxalate particles made using this synthesis technique i.e. that by
207 Watkinson et al., were lath-shaped in morphology [4]. This morphology was also expected for the
208 oxides [10]. It was thus possible that the particles could have had a preferred orientation if packed in
209 a recessed sample holder for PXRD. However, the sample was instead sprinkled on a silicon crystal in
210 order to minimise the effect in the subsequent diffraction data. The PXRD data were refined well (see
211 Table 1) without the need for texture corrections. A March-Dollase model for preferred orientation
212 was not found to further improve the fit. This also suggested a lack of texture in the sample. The Popa
213 model [14] was used to test if the crystallite size and microstrain distributions fitted an anisotropic
214 model. The result suggested that the crystallites were essentially isotropic, and therefore spherical,
215 and that the crystallites experienced isotropic microstrain. These results are presented in Table 1. The
216 spherical crystallite conclusion corroborated with the lack of texture observed in the PXRD data.

217 Table 2 shows that atomic position parameters refined using both approaches are similar to one
218 another and are consistent with the results of Chakraborty et al [13]. The cation-anion bond lengths
219 are shown in Table 3. Although the Ce1-O2 and Nd1-O2 bond lengths are larger than those of the
220 other bond lengths shown in Table 3, they are consistent with the M1-O2 bond lengths reported for
221 another lanthanide mixed oxide, namely, $La_3Gd_{1-x}Ce_xO_{1.5+(x/2)}$ reported by Grover et al. [16].

222 Table 2 shows that refining a single (general) isotropic displacement parameter (Biso) for the cations
223 resulted in a physically meaningful value that had reduced precision when compared to the results of
224 Chakraborty et al [13], which agrees with expectation given that Chakraborty et al. [13] used a neutron
225 source for their diffraction experiments.

226 Both refinements of this study resulted in large oxygen occupancies as shown in Table 2. Each
227 corresponded to oxygen-to-metal ratios of around 1.5 to 2 s.f. (specifically, 1.53 and 1.48 to 3 s.f. for
228 the refinement that refined a general Biso for cations and the refinement that used the cation Biso
229 values of Chakraborty et al [13]). According to the notation of the Ce Nd oxide solid solutions, namely,
230 $Ce_{1-x}Nd_xO_{2-(x/2)}$, an oxygen-to-metal ratio of around 1.695 was expected for each refinement based on
231 an x value of 0.61. The refined oxygen-to-metal ratios are therefore not meaningful. In order to assess
232 the impact of using oxygen occupancies that corresponded to an expected oxygen-to-metal ratio of
233 1.695, O1 and O2 occupancies values of 0.94 and 0.57 were fixed for each of the refinements. The
234 result was an increase in the O2 fractional atomic positions (x,y,z) to large values i.e. 0.4208(8) for all
235 three coordinates for the refined general isotropic displacement parameter approach refinement and
236 0.4165(8) for all three coordinates for refinement that used the cation Biso values of Chakraborty et
237 al [13]. Each of these refinements resulted in an increase in the Ce1-O2 and Nd1-O2 bond lengths to
238 non-reasonable values i.e. to 3.26 Å each for the first refinement approach, and to 3.17 Å for the
239 second refinement approach. However, the lattice parameters were consistent with the previous
240 refinements.

241 The results suggest that refinement of the structure of the Ce Nd oxide using X-rays is limited. Yet, all
242 refinements have resulted in similar lattice parameters values to 6 s.f. i.e. 11.0220 Å. The average of
243 the lattice parameters presented in Table 1 is 11.02201(6) Å where the number in the parenthesis is
244 the combined effect of the two standard deviations. Thus this study has achieved one of its key
245 objectives, namely, to estimate the lattice parameter of the material with greater precision than that
246 achieved previously by fitting Gaussian profiles to diffraction peaks [4]. By conducting a Rietveld

247 refinement, it was possible to account for the instrument's contribution to the PXRD data to allow a
248 more precise estimate to be achieved. The material can now undergo sintering studies and the impact
249 of the sintering environment of the lattice parameter, and hence the oxygen-to-metal ratio can be
250 determined. This is particularly important for the ESA radioisotope power systems programme, where
251 the impact of the sintering environment of the fuel's composition will need to be established.
252 Additionally, the variation in the crystallography of the different surrogates and americium oxides will
253 need to be compared. It is important to highlight that from a practical perspective any diffraction
254 experiments with americium oxides are likely to be conducted with an X-ray diffractometer that would
255 be contained within a glovebox. Thus it is likely that there will be similar constraints in the refinement
256 of the crystallography of americium oxides as has been found here with the refinement Ce Nd oxides
257 using X-rays.

258 Figure 2a and 2b show that the lattice parameter of the oxide is consistent with a $Ce_{1-x}Nd_xO_{2-(x/2)}$ solid
259 solution with an x value of ~ 0.6 . The solution of the quadratic Equation 1 confirmed this. The
260 uncertainty in Equation 1, and therefore in the uncertainty in the solution, cannot be commented on
261 quantitatively. However, it is not unreasonable to make this qualitative assessment of consistency,
262 particularly if the deviation in the experimental data of Horlait et al. [10] from the plotted Equation 1
263 in Figure 2b is considered as an indication of the uncertainty (see the x equal to 0.59 and 0.675 data
264 points in Figure 2b). This Rietveld refinement study to determine the lattice parameter of such an
265 oxide confirms that an x value of ~ 0.602 has been achieved and is thus corroborates with the assumed
266 quantitative XRF value of 0.61(1). The half-value of the refined lattice parameter is also consistent
267 with this expected ratio. This Rietveld refinement study has therefore met its second key objective.

268 **5 Conclusion**

269 The lattice parameter of synthesised Ia-3 $Ce_{1-x}Nd_xO_{2-(x/2)}$ with an assumed Nd/[Ce+Nd] ratio of 0.61
270 was determined by Rietveld refinement. Rietveld refinement of the X-ray diffraction pattern has
271 enabled a more precise estimate of the lattice parameter to be determined than was previously
272 achieved using Gaussian peak fitting [4]. The study corroborates with the assumed QXRF inferred x
273 value of 0.61 of a previous study [4]. The lattice parameter has been determined in preparation for
274 future oxide sintering studies as part of the ESA radioisotope powers systems programme. This data
275 is essential as variations in the oxygen-to-metal ratio and crystallography (specifically lattice
276 parameters as this will relate to volume changes) caused by different sintering conditions will want to
277 be investigated. Changes in the ratio for an Fm-3m or Ia-3 $Ce_{1-x}Nd_xO_{2-(x/2)}$ can be inferred by changes
278 in lattice parameter. Thus such investigations can be pursued now that the non-sintered input
279 material has been characterised.

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283 **Data availability**

284 The raw data required to reproduce these findings cannot be shared at this time due to technical or
285 time limitations. The processed data required to reproduce these findings cannot be shared at this
286 time due to technical or time limitations.

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