

Detailed X-ray diffraction analysis of $Ce_{1-x}Nd_xO_{2-(x/2)}$ as a surrogate for substoichiometric americium oxide



E.J. Watkinson^{a,*}, D. Chateigner^c, R.M. Ambrosi^a, S. Gascoin^c, H.R. Williams^b, K. Stephenson^d

^a Department of Physics and Astronomy, University of Leicester, University Road, Leicester, LE1 7RH, United Kingdom

^b Department of Engineering, University of Leicester, University Road, Leicester, LE1 7RH, United Kingdom

^c Normandie Université, IUT-Caen, Université de Caen Normandie, CNRS, CRISMAT-ENSICAEN, Caen, France

^d European Space Agency, ESTEC TEC-EP, Keplerlaan 1, 2201AZ, Noordwijk, The Netherlands

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ABSTRACT

European Space Agency (ESA) radioisotope power systems will use ^{241}Am 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.

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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 ^{241}Am 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 pellets [4]. The characterisation of the oxide powders prior to their sintering is thus essential to these studies.

One of the americium oxides of interest to the ESA programme is a substoichiometric form, namely, Ia-3 $\text{AmO}_{2-(x/2)}$. In a previous

* Corresponding author.

E-mail address: ejw38@le.ac.uk (E.J. Watkinson).

study, Ia-3 (C-type) $Ce_{1-x}Nd_xO_{2-(x/2)}$ with x values between 0.5 and 0.7 were proposed as candidate surrogates for certain Ia-3 $AmO_{2-(x/2)}$ [4]. A synthesis method where Ce Nd oxalates were continuously co-precipitated from the reaction of Ce and Nd nitrate and oxalate feeds was used. The oxalates were then calcined to form $Ce_{1-x}Nd_xO_{2-(x/2)}$. An x value of 0.60 was targeted by mixing the metal nitrates in an appropriate corresponding molar ratio [4]. Powder X-ray diffraction (PXRD) and Raman spectroscopy analyses confirmed the synthesis of Ia-3 $Ce_{1-x}Nd_xO_{2-(x/2)}$ material [4]. Additionally, quantitative X-ray fluorescence (QXRF) established that each material was made with a reproducible $Nd/[Ce + Nd]$ ratio of 0.62 with a coefficient of variation of around 0.1% [4] and its uncertainty was estimated to be ± 0.01 . It has since been noticed that a slight numerical oversight was made in the previous paper [4]. The x value should have been stated as 0.61 with a coefficient of variation of around 0.1% and an estimated uncertainty of ± 0.01 . Thus the QXRF analysis confirmed that this co-precipitation method can be used to target an x value for a Ce Nd based oxide solid solution.

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

The relationship developed by Horlait et al. [10] for the $Ce_{1-x}Nd_xO_{2-(x/2)}$ system up to x equal to 0.73 relates the lattice parameter, a , and x by a quadratic equation, namely,

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

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

In the previous study by Watkinson et al. [4], an initial estimate of the lattice parameter of the synthesised Ia-3 $Ce_{1-x}Nd_xO_{2-(x/2)}$ (with a 0.62 $Nd/[Ce + Nd]$ ratio) was determined to be $5.51 \text{ \AA} \pm 0.01 \text{ \AA}$ (Note that this estimate did not rely on the value of

the ratio and is thus unaffected by the ratio being corrected to 0.61.). This was calculated from the 2θ positions of specific diffraction peaks, which were determined by fitting Gaussian profiles to them. Additionally, Equation (1) was used to predict 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 0.62. This was confirmed to be 5.51 \AA to 3 s. f. For completeness, the lattice parameter for a $Ce_{1-x}Nd_xO_{2-(x/2)}$ phase with the corrected x value of 0.61 has been calculated: 5.51 \AA to 3 s. f. The predicted lattice parameter was thus consistent with the estimate made by the aforementioned peak position procedure.

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

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

2. Method

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

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

The MAUD (Materials Analysis Using Diffraction) programme was used to Rietveld refine the diffraction data [11]. The NIST LaB6 SRM660b standard powder was used to refine the instrumental contribution (peak width evolution with 2θ , peak shapes and

Gaussian-Lorentzian components, z-displacement parameter). A Crystallography Open Database (COD) [12] file, namely, COD 1548619, for Ia-3 $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ by Chakraborty et al. [13] was used as the starting phase file. Although their diffraction data were recorded using a neutron source, it provided an initial starting point for the analysis by providing nominal values for the cell parameter, occupancy, fractional atomic positions (x,y,z) and isotropic atomic displacement parameters (B_{iso}) of the analysis.

The zeroth order background term and overall scale factor were initially visually estimated. The background was then modelled using a 4th degree polynomial. Further increase of the polynomial order did not improve the refinement. The analysis first proceeded with the refinement of the intensity scale and unit cell parameter, followed by the 2θ offset. The isotropic crystallite size parameter was refined and a default microstrain value of 6×10^{-4} was assumed. In an attempt to establish the impact of an anisotropic mean size on the refinement, the Popa model [14] was employed where the zeroth (isotropic) and then the first order parameters were refined. This was followed by the zeroth and first order microstrain terms for the Popa model [14]. The reader is referred to an introductory overview of the Popa model [15]. As Ce and Nd ions have similar atomic numbers, it was unlikely that the X-ray diffraction data would be able to refine the occupancies of the Nd and Ce ions. The occupancies of the Ce and Nd ions were fixed according to the $\text{Nd}/[\text{Ce} + \text{Nd}]$ ratio of 0.61 (see the bottom half of Table 2). The refined structural parameters of $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ by Chakraborty et al. [13] were consulted to identify the fractional atomic positions that were permitted to vary in Ia-3 (C-type) $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$. For convenience, their structural data are stated in the top half of Table 2. As X-rays are less sensitive in the determination of B_{iso} parameters than neutrons, the B_{iso} values of all atoms were assumed to be the same as Chakraborty et al. [13] who refined neutron diffraction data.

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

3. Results

Fig. 1 illustrates the recorded and the refined PXRD patterns of the analysed $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ material using the two approaches for isotropic atomic displacement parameters (B_{iso}) of the cations. The refined cell and structural parameters are outlined in Table 1 and Table 2, respectively. The bond distances between the cations and anions for each model are shown in Table 3. The half-value of the refined lattice parameters were both thus 5.51101 (4) Å. The relationship between the lattice parameter and the x value for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system (for x values up to 0.73) that was developed by Horlait et al. [10], namely, Equation (1), is shown in Fig. 2. The figure also illustrates their experimental data [10]. The half-value of the lattice parameters refined in this study are plotted as a single point in each of Fig. 2a–b where the x value was assumed to be 0.61 (1) according to Watkinson et al. [4], for the purpose of plotting. Additionally, the quadratic Equation (1) was solved for x using the half-value of the refined lattice parameters, namely, 5.51101 (4), to provide a more precise estimate of the x value of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$

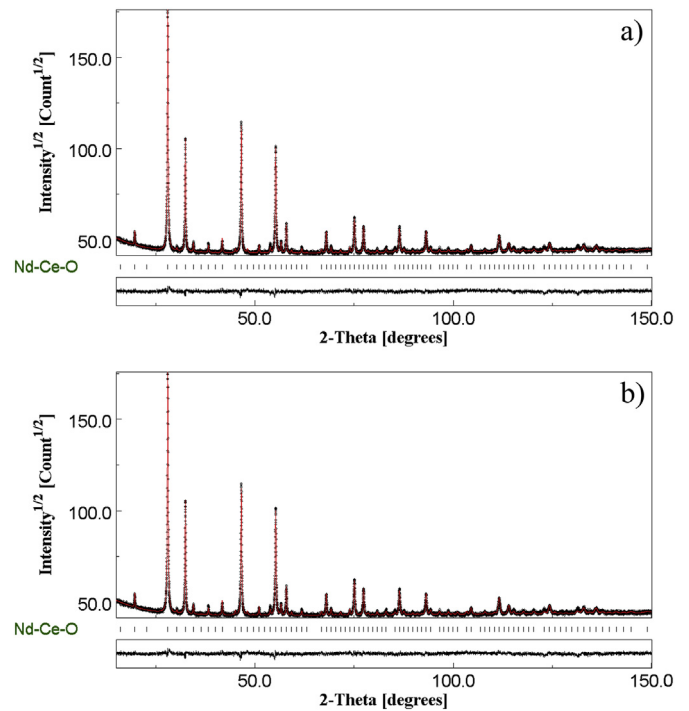


Fig. 1. Illustrates the experimental PXRD pattern for the synthesised Ia-3 $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ (black circles); the Rietveld refined pattern (red line) and the residuals of the fit (a) when a general B_{iso} parameter was refined for the cations and (b) when the cation B_{iso} values of Chakraborty et al. [13] were used. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

The refined parameters and associated data. The values in brackets are the estimated standard 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 ($^\circ$)	-0.0041 (3)
Average crystallite size (Å)	462 (1)
Microstrain	$6.33 (6) \times 10^{-4}$
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, a (Å)	11.02202 (8)
2θ offset ($^\circ$)	-0.0041 (3)
Average crystallite size (Å)	464 (1)
Microstrain	$6.50 (6) \times 10^{-4}$
R_{wp} (%)	2.39
R_{exp} (%)	2.19
Goodness of Fit	1.09

2) material. The solution was an x value of 0.602 (when the uncertainties in a were considered the uncertainty in x was +0.001/-0.000 to 3. s.f).

As was stated in the Introduction, the lattice parameter of a $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ phase with the corrected x value of 0.61 was predicted using Equation (1) to be: 5.51 Å to 3 s. f. The result was consistent with the lattice parameter estimates from peak position estimates determined by Gaussian curve fits to diffraction peaks [4]. As this Rietveld refinement study has enabled the lattice parameter to be

Table 2

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

Atom	Site	X	Y	Z	B_{iso} (\AA^2)	Occupancy
Chakraborty et al. [13].						
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	8 b	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)

Table 3

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

Atomic Site	Atomic Site	Atomic Bond Distance (\AA)	
		Refinement with a general isotropic displacement parameter for cations.	Refinement that used Chakraborty's isotropic displacement parameter for cations [13].
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

determined more precisely, the predicted value is stated to a greater number of significant figures i.e. 5.512 (1) \AA to 4 s. f. for comparison. This states the uncertainty in the predicted lattice parameter associated with the estimated uncertainty in the assumed QXRF value.

4. Discussion

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

It was previously observed that oxalate particles made using this synthesis technique i.e. that by Watkinson et al. were lath-shaped in morphology [4]. This morphology was also expected for the oxides [10]. It was thus possible that the particles could have had a preferred orientation if packed in a recessed sample holder for PXRD. However, the sample was instead sprinkled on a silicon crystal in order to minimise the effect in the subsequent diffraction data. The PXRD data were refined well (see Table 1) without the

need for texture corrections. A March-Dollase model for preferred orientation was not found to further improve the fit. This also suggested a lack of texture in the sample. The Popa model [14] was used to test if the crystallite size and microstrain distributions fitted an anisotropic model. The result suggested that the crystallites were essentially isotropic, and therefore spherical, and that the crystallites experienced isotropic microstrain. These results are presented in Table 1. The spherical crystallite conclusion corroborated with the lack of texture observed in the PXRD data.

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

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

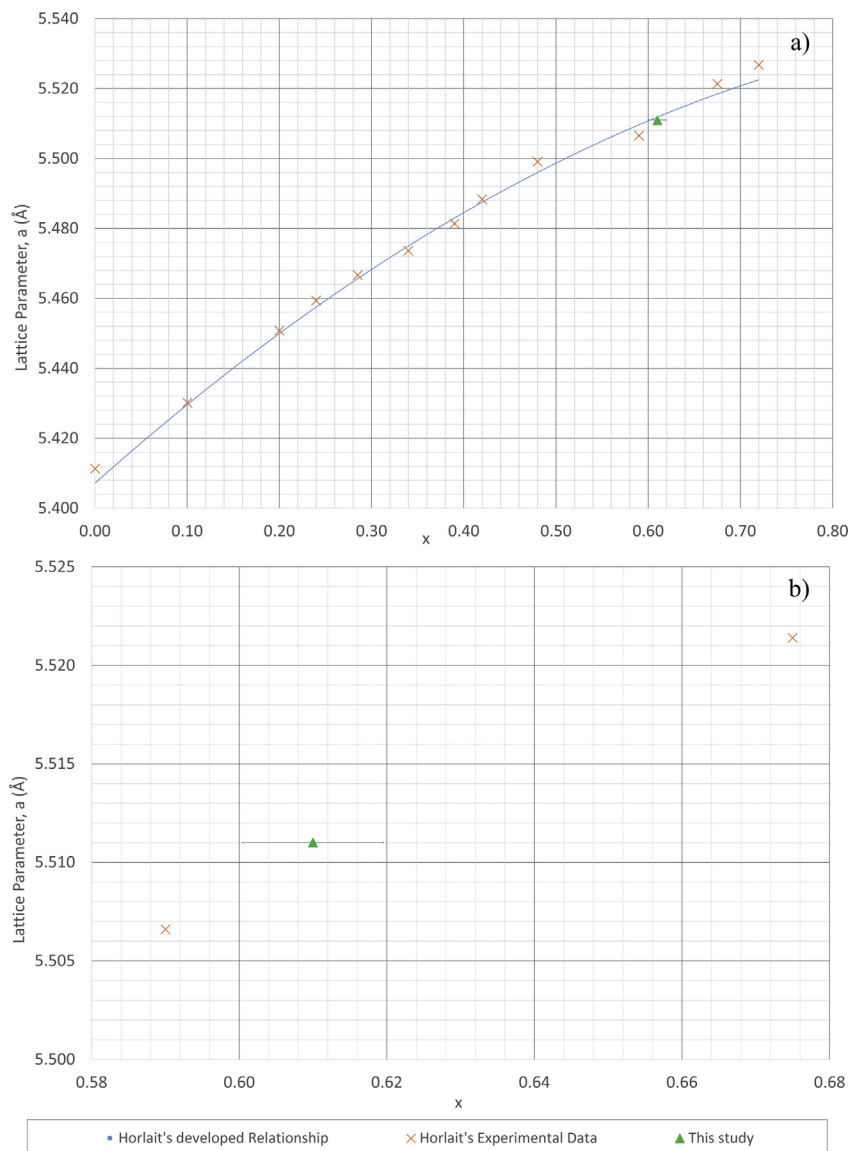


Fig. 2. Illustrates the lattice parameter- x relationship developed by Horlait et al. [10] for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$ system (solid blue line) with their experimental (red cross) data illustrated. The lattice parameter (triangle) determined for the oxide synthesised in this study is consistent with the data. The material is assumed to have an x value and uncertainty of 0.61 (1) [4]. a) Illustrates the data over the entire x -range over which the Horlait et al. [10] relationship is valid and b) over x values near 0.61. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Both refinements of this study resulted in large oxygen occupancies as shown in Table 2. Each corresponded to oxygen-to-metal ratios of around 1.5–2 s. f. (specifically, 1.53 and 1.48–3 s. f. for the refinement that refined a general Biso for cations and the refinement that used the cation Biso values of Chakraborty et al. [13]). According to the notation of the Ce Nd oxide solid solutions, namely, $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-(x/2)}$, an oxygen-to-metal ratio of around 1.695 was expected for each refinement based on an x value of 0.61. The refined oxygen-to-metal ratios are therefore not meaningful. In order to assess the impact of using oxygen occupancies that corresponded to an expected oxygen-to-metal ratio of 1.695, O1 and O2 occupancies values of 0.94 and 0.57 were fixed for each of the refinements. The result was an increase in the O2 fractional atomic positions (x,y,z) to large values i.e. 0.4208 (8) for all three coordinates for the refined general isotropic displacement parameter approach refinement and 0.4165 (8) for all three coordinates for refinement that used the cation Biso values of Chakraborty et al.

[13]. Each of these refinements resulted in an increase in the Ce1-O2 and Nd1-O2 bond lengths to non-reasonable values i.e. to 3.26 Å each for the first refinement approach, and to 3.17 Å for the second refinement approach. However, the lattice parameters were consistent with the previous refinements.

The results suggest that refinement of the structure of the Ce Nd oxide using X-rays is limited. Yet, all refinements have resulted in similar lattice parameters values to 6 s. f. i.e. 11.0220 Å. The average of the lattice parameters presented in Table 1 is 11.02201 (6) Å where the number in the parenthesis is the combined effect of the two standard deviations. Thus this study has achieved one of its key objectives, namely, to estimate the lattice parameter of the material with greater precision than that achieved previously by fitting Gaussian profiles to diffraction peaks [4]. By conducting a Rietveld refinement, it was possible to account for the instrument's contribution to the PXRD data to allow a more precise estimate to be achieved. The material can now undergo sintering studies and the

impact of the sintering environment of the lattice parameter, and hence the oxygen-to-metal ratio can be determined. This is particularly important for the ESA radioisotope power systems programme, where the impact of the sintering environment of the fuel's composition will need to be established. Additionally, the variation in the crystallography of the different surrogates and americium oxides will need to be compared. It is important to highlight that from a practical perspective any diffraction experiments with americium oxides are likely to be conducted with an X-ray diffractometer that would be contained within a glovebox. Thus it is likely that there will be similar constraints in the refinement of the crystallography of americium oxides as has been found here with the refinement Ce Nd oxides using X-rays.

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

5. Conclusion

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

Data availability

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

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