Fergusonite-type $\text{CeNbO}_{4+\delta}$: single crystal growth, symmetry revision and conductivity

Bayliss, Ryan D.; Pramana, Stevin S.; An, Tao; Wei, Fengxia; Skinner, Stephen J.; White, Timothy John; Baikie, Tom; Kloc, Christian; White, Andrew J. P.

2013

Bayliss, R. D., Pramana, S. S., An, T., Wei, F., Kloc, C., White, A. J., Skinner, S. J., White, T. J., & Baikie, T. (2013). Fergusonite-type $\text{CeNbO}_{4+\delta}$: Single crystal growth, symmetry revision and conductivity. *Journal of solid state chemistry*, Vol 204, 291-297.

<https://hdl.handle.net/10356/100393>

<https://doi.org/10.1016/j.jssc.2013.06.022>

© 2013 Elsevier. This is the author created version of a work that has been peer reviewed and accepted for publication by *Journal of Solid State Chemistry*, Elsevier. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: <http://dx.doi.org/10.1016/j.jssc.2013.06.022>.

Downloaded on 26 Apr 2023 18:47:09 SGT

Fergusonite-Type $\text{CeNbO}_{4+\delta}$: Single Crystal Growth, Symmetry Revision and Conductivity

Ryan D. Bayliss,^a Stevin S. Pramana,^b Tao An,^b Fengxia Wei,^b Christian L. Kloc,^b Andrew J. P. White,^c Stephen J. Skinner,^a Timothy J. White^b and Tom Baikie,^{b*}

^a Department of Materials, Imperial College London, Prince Consort Road, London, SW7 2BP, United Kingdom

^b School of Materials Science & Engineering, 50 Nanyang Avenue, Nanyang Technological University, Singapore, 639798

^c Chemical Crystallography Laboratory, Department of Chemistry, Imperial College London, Exhibition Road, London, SW7 2AZ, United Kingdom

*Corresponding author – tbaikie@ntu.edu.sg

Abstract

Large fergusonite-type (ABO_4 , $A = \text{Ce}$, $B = \text{Nb}$) oxide crystals, a prototype electrolyte composition for solid oxide fuel cells (SOFC), were prepared for the first time in a floating zone mirror furnace under air or argon atmospheres. While CeNbO_4 grown in air contained $\text{CeNbO}_{4.08}$ as a minor impurity that compromised structural analysis, the argon atmosphere yielded a single phase crystal of monoclinic CeNbO_4 , as confirmed by selected area electron diffraction, powder and single crystal X-ray diffraction. The structure was determined in the standard space group setting $C12/c1$ (No. 15), rather than the commonly adopted $I12/a1$. AC impedance spectroscopy conducted under argon found that stoichiometric CeNbO_4 single

crystals showed lower conductivity compared to $\text{CeNbO}_{4+\delta}$ confirming interstitial oxygen can penetrate through fergusonite and is responsible for the higher conductivity associated with these oxides.

1. Introduction

Ceramics with oxygen hyper-stoichiometry have garnered attention as potential solid oxide fuel cell electrolytes due to their lower activation energy for mobilisation of interstitial oxide ions, compared to the extensively studied fluorite and perovskite systems that are oxygen deficient [1]. Some examples of ‘intermediate’ temperature electrolytes (500-700°C) include doped and undoped lanthanide silicate and germanate apatites (e.g. $\text{La}_{9.33}(\text{Si/Ge})_6\text{O}_{26}$) [2], melilites such as $\text{La}_{1+x}\text{Sr}_x\text{Ga}_3\text{O}_{7+x/2}$ [3], and cuspidine-types including $\text{Nd}_4(\text{Ga}_{1.4}\text{Ge}_{0.6}\text{O}_{7.3})\text{O}_2$ [4]. Additionally, promising results have been obtained from interstitial-containing mixed electronic ionic conducting (MEICs) oxides, a good example being $\text{La}_2\text{NiO}_{4+\delta}$ materials and related higher order phases [5]. Another well studied MEIC family are the $\text{CeNbO}_{4+\delta}$ series that when crystallised as the low temperature fergusonite-type ($T < 750^\circ\text{C}$), exhibit rapid oxide ion diffusion as shown via ^{18}O exchange [6]. At ambient temperature, four compositionally discrete crystal structures have been identified - CeNbO_4 , $\text{CeNbO}_{4.08}$, $\text{CeNbO}_{4.25}$ and $\text{CeNbO}_{4.33}$ [7, 8]. However, only the stoichiometric CeNbO_4 has been completely described crystallographically at room temperature in a monoclinic cell [9],[10], with a tetragonal scheelite-type polymorph characterised above 750°C [10]. As a result of their complexity none of the phases containing interstitial oxygen have been structurally refined, however, electron microscopy shows they alternate between commensurately and incommensurately modulated superstructures [7], with the incorporation of excess oxygen accompanied by oxidation of Ce^{3+} to Ce^{4+} as shown by XANES measurements [11-13].

Rietveld refinement of the cerium niobate powder diffraction patterns containing evidence of long range modulation is challenging, due to the difficulty of deconvoluting large numbers of overlapping and weak supercell reflections that often lead to unconvincing refinements with respect to bond valence sums. Although no single crystal structural work has been published, a laser heated pedestal growth technique produced an appreciable CeNbO₄ crystal, that was reduced to powder to establish phase purity, and a full structure determination was not attempted [14].

In this work, single crystals of CeNbO₄ were characterised by selected area electron diffraction, powder and single-crystal X-ray diffraction. The crystals were grown in air or argon. The first condition led to a biphasic assemblage of CeNbO₄ and minor CeNbO_{4+δ} ($\delta = 0.08$), that prevented an unambiguous structure determination by XRD. Under argon, single phase CeNbO₄ crystals conformed to *C*12/*c*1 (No. 15) symmetry, which is the standard setting of the pseudo-tetragonal *I*12/*a*1 cell commonly used; the former is a maximal non-isomorphic subgroup of tetragonal *I*4₁/*a* (No. 88). In carrying out the conversion of *C*12/*c*1 to *I*12/*a*1 we found several previous reports incorrectly transformed the lattice metric with *a* and *c* interchanged. Similarly, the chemical analogue LaNbO₄ [15], has been reported as *I*12/*a*1 but subsequently corrected to *I*12/*c*1 after deposition in the inorganic crystal structure database (card number 173632) [16]; however, the entry for the CeNbO₄ analogue has not been so amended.

2. Experimental

2.1 Preparation of Single Crystals of CeNbO₄

Commercial powders of CeO₂ (Merck, 99.9%) and NbO₂ (Aldrich, 99.99%) were mixed in stoichiometric proportions and calcined in a box furnace at 1000°C for 12 hours. After grinding, the powder was pressed into a rod under a hydrostatic pressure (100 MPa) and sintered (1400°C/ 16 h/ air).

Crystal growth took place in an optical floating zone furnace (Crystal Systems Corporation, Japan - Model number: FZ-T-4000-H-VPO-VII-PC) where four ellipsoidal mirrors with 700W halogen lamps were the infrared sources. The critical synthesis conditions were: melt translation (10mm/h), counter rotation rate (40 rpm) for the feed and seed rods, and atmosphere (flowing air or argon gas at 2L/min). When the crystals emerge from the molten zone and cool they pass through the tetragonal to monoclinic phase transition at approximately 750°C [12], which induces stress, sometimes accompanied by cracking due to the change in specific volumes (monoclinic = 324.86(2) Å³ (this work); tetragonal = 335.22 Å³) [10].

2.2 Powder X-ray Diffraction (XRD)

Sample purity was established using powder X-ray diffraction with separate patterns collected at room temperature from each end of the as-grown rods. Data were gathered using a Bruker D8 Advance diffractometer fitted with a CuK_α source operated at 40kV and 40mA, a 1° divergence slit, 0.3mm receiving slit, a secondary graphite monochromator and a Lynxeye silicon strip detector. Manually crushed powders were mounted in a top-loaded trough and data accumulated from 10 – 130° 2θ using a step size of 0.02° with a dwell time of 2s per step. The sample holder was rotated at 30 rpm during acquisition. Rietveld refinement was carried out with TOPAS *V4.1*¹⁴ using the fundamental parameters approach [17] and a full axial divergence model [18]. The specimen-dependent parameters refined

were the zero error, the Chebyshev polynomial fitting coefficients of the background, and the ‘crystallite size’ to model microstructure-controlled line broadening. The starting model for the refinement was transferred from the crystal structure derived from single-crystal X-ray diffraction.

2.3 Single Crystal X-ray Diffraction

Crystals were cleaved from the as-grown rod for analysis by single crystal X-ray diffraction. Data were collected at 100K with a Bruker Smart Apex II three-circle diffractometer using graphite monochromated Mo- $K\alpha$ radiation over the angular range $5 - 55^\circ 2\theta$. An empirical absorption correction was applied and the refinements were carried out with Jana 2006 [19] utilising the Superflip [20] structure solution algorithm. All atomic positions were refined using anisotropic displacement parameters (ADPs) and three-dimensional Fourier maps were generated with VESTA [21].

2.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy was conducted on powders deposited on holey-carbon copper grids and loaded in an analytical double tilt holder. Data were obtained at 200kV using a JEOL JEM-2100 electron microscope ($C_s = 0.5\text{mm}$) equipped with an EDAX EDS X-ray microanalysis system and three field-limiting apertures for selected-area electron diffraction (SAED; 5, 20 and 60 mm diameter). High resolution images were collected using an objective aperture ($100\mu\text{m}$), corresponding to a nominal point-to-point resolution of $\sim 1.7 \text{ \AA}$. Electron diffraction patterns were calibrated against external standards to derive reliable values for both the electron wavelength and camera length. Lattice parameters were

determined repeatedly to check for hysteresis of the electromagnetic lenses leading to errors $< \pm 1\%$.

2.5 Differential Thermal Analysis/Thermogravimetric Analysis (DTA/TGA)

Changes in the oxygen stoichiometry of all samples were determined from thermogravimetric analysis in flowing air (50 ml/h) using a Netzsch STA 449C Jupiter simultaneous TG-DTA/DSC instrument in the temperature range of 20-1000°C with a heating/cooling rate of 10°C/min. Data were collected from a fine powder mechanically ground from a section of the single crystal sample.

2.6 Electrochemical Impedance Spectroscopy (EIS)

AC impedance spectroscopy measurements were performed in the temperature range of 150°C to 600°C in flowing argon that was free of oxygen. The response was measured using a Solartron 1260 frequency response analyser between 0.01 Hz and 1 MHz with amplitude of 100 mV. Silver electrodes were painted on to the single crystals and fired to remove organics and ensure good adhesion at 700 °C for 2 hours. Each electrode was held in good contact with platinum mesh contacts by a spring loaded ceramic plunger. Electrical measurements were made via platinum wires attached to platinum mesh contacts. After the spectra were corrected for sample geometry and fitted to a basic model using the ZView software (Scribner Associates), the bulk ($\sim 10^{-12}$ F) and electrode ($\sim 10^{-7}$ F) responses were assigned from their capacitance values [22]. As expected, no grain boundary response was observed from the single crystal. The high frequency intercept of the electrode arc with the x -axis was used as a value for total sample resistivity.

3. Results and discussion

3.1 Crystal Preparation and Preliminary Structural Characterisation

The molten zone of the cerium niobate was viscous and growth proceeded in a very stable manner, yielding a dark green, opaque mass approximately 20mm long (Figure 1). XRD patterns from the top and bottom rod sections were indistinguishable; however, those obtained from air and argon atmospheres were distinct. When the crystals were reduced to a powder the argon grown sample was yellow, whereas the crystal grown in air was green reflecting the partial oxidation of cerium. From the crystal grown in air the powder XRD reflections obtained matched those reported by Santoro *et al.* [9] and showed stoichiometric CeNbO_4 had been successfully grown, however the crystal also contained weak reflections assigned to the incommensurately modulated $\text{CeNbO}_{4.08}$ (Figure 2), but this could not be assessed by quantitative phase analysis as a satisfactory model was unavailable. Nonetheless, the relative intensities confirm an abundance of the stoichiometric phase. By contrast, no additional reflections were evident in the argon grown sample and Rietveld refinement confirmed this material to be compositionally pure CeNbO_4 within the instrumental detection limit (Figure 3).

3.2 Crystal Structure Analysis

It proved impossible to select a single pure CeNbO_4 crystal from the air grown ingot. Although the unit cell metric agreed with the reported values [9], structure refinements led to high R values ($R = 0.0865$; $wR = 0.1988$; $\text{GoF} = 3.94$) and the Fourier maps contained

features at unreasonably close distances to the Nb (≈ 1.24 Å) and Ce (≈ 0.95 Å) that were not physically meaningful. In addition, the total number of observed reflections were far fewer than typically expected for a low symmetry cell (air = 547, argon = 773). Inspection of the yellow crystals under a polarising light microscope showed dark green veins suggesting zoning of the oxidised phase, whose green colour intensifies as more interstitial oxygen is incorporated into the structure [7].

In contrast, structure determination of the argon grown crystal was straightforward; data collected at 100 K were readily accommodated in the $C12/c1$ space group. The standard space group $C12/c1$ corresponds to that used for the fergusonite prototype (YVO_4) [23]. On transformation to the pseudo-tetragonal $I12/a1$ setting, commonly used for direct comparison with the high temperature tetragonal $I4_1/a$ scheelite-type polymorph of $CeNbO_4$, it was noted that the a and c lattice parameters took opposing values to those published [9]. Specifically, the $I12/a1$ setting must have the cell parameters $a = 5.1621(4)$ Å, $b = 11.4030(5)$ Å $c = 5.5365(2)$ Å and $\beta = 94.594(11)^\circ$, to meet the prescribed requirement for the shortest cell parameter being the a direction. It is noted that earlier reports are incorrect and lead to a glide plane being assigned to the wrong direction. The setting used in this work is consistent with $LaNbO_4$ with $a = 5.2042(8)$ Å, $b = 11.521(4)$ Å, $c = 5.5682(9)$ Å and $\beta = 94.09(1)^\circ$ [24]. Figure 4 graphically illustrates the symmetry relationship between the $I12/a1$ and $C12/c1$ cells for $CeNbO_4$. The matrix transforming the atomic positions of a tetragonal (subscript t) scheelite-type cell to an I centred monoclinic cell (subscript mI) is:

$$\begin{pmatrix} a_{mI} \\ b_{mI} \\ c_{mI} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_t \\ b_t \\ c_t \end{pmatrix}$$

$$\begin{pmatrix} x_{mI} \\ y_{mI} \\ z_{mI} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_t \\ y_t \\ z_t \end{pmatrix}$$

The unit cell and atomic coordinate transformation matrices for the pseudo-tetragonal, monoclinic $I12/a1$ (subscript mI) to the standard $C12/c1$ (subscript mC) space group setting are:

$$\begin{pmatrix} a_{mC} \\ b_{mC} \\ c_{mC} \end{pmatrix} = \begin{pmatrix} -1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_{mI} \\ b_{mI} \\ c_{mI} \end{pmatrix}$$

$$\begin{pmatrix} x_{mC} \\ y_{mC} \\ z_{mC} \end{pmatrix} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} x_{mI} \\ y_{mI} \\ z_{mI} \end{pmatrix}$$

The proliferation of erroneous descriptions of fergusonite-type crystallography highlights the importance of carrying out single crystal diffraction experiments, where the higher precision resulting from the use of symmetry-equivalent reflections brought the transformational anomaly to our attention; several powder studies failed to reveal the erroneous symmetry settings [8, 9]. Figure 5 shows a polyhedral representation highlighting the structural relationship between the tetragonal ($I4_1/a$) scheelite-type structure and the I and C centred monoclinic cells for CeNbO_4 . Tables 1 and 2 collate the refined atomic positions and selected bond distances in $C12/c1$, while Table 3 shows the refined equivalent cell parameters and atomic positions for $I12/a1$. Table 1 also contains the data collection parameters and agreement indices. The highest residual electron density peak of $+4.73 \text{ e}/\text{\AA}^3$ slightly exceeds what generally is acceptable and inspection of the difference Fourier maps contain strong peaks of electron density near Ce ($0.5 - 0.6 \text{ \AA}$) and Nb ($0.1 - 0.7 \text{ \AA}$) at physically impossible

distances (Figure 6). The additional electron density was present in all crystals but the origin of these features remains unclear, though it is possibly related to an imperfect absorption correction performed on the single crystal. No clear interstitial oxygen sites are evident in the difference Fourier maps, though CeNbO_4 is known to readily oxidise at low temperatures. It is likely that if there were interstitial oxygen present then it was below the minimum needed ($\delta = 0.08$) to produce the first order incommensurate supercell reflections previously observed in $\text{CeNbO}_{4.08}$ [7]. Rocking curve analysis yields narrow diffraction peaks that confirm the Fourier map features do not arise from poorly formed crystals containing unusual mosaicity and/or domain features. The Full Width Half Maximum (FWHM) for CeNbO_4 ($0.18^\circ 2\theta$) (Figure 7), is expected for a high quality crystal and is comparable to recently reported apatite-type SOFC electrolytes prepared in a similar way [25]. Further work is now underway to probe the local structure of the Ce and Nb sites in these phases.

The high resolution TEM (HRTEM) image shows a well ordered crystal with thickness fringes (Figure 8a). The $[101]_{mC} \equiv [001]_t$ selected area diffraction patterns (SAED) (Figure 8b) ($d_{020} = 0.57\text{nm}$, $d_{\bar{1}11} = 0.47\text{nm}$ and $d_{\bar{2}02} = 0.26\text{nm}$) did not reveal any additional supercell reflections, as would be anticipated for stoichiometric CeNbO_4 .

3.3 Thermogravimetric Analysis/Differential Thermal Analysis

The TGA/DTA heating curve is similar to that reported by Packer *et al.* [12], but additionally the cooling curve is also included here (Figure 9). From approximately 250°C (labelled A) the weight increases (interstitial oxygen incorporation) and reaches a maximum at 550°C , before a sharp drop at 730°C (labelled B); an event coinciding with a small endothermic peak associated with the monoclinic to tetragonal phase transition and loss of the interstitial oxygen content [8]. Above 745°C up until 1000°C the structure remains stoichiometric

CeNbO₄ within the detection limits of the equipment. The jump in the DSC data (labelled C) at 1000°C is an artefact of the equipment and is associated with a heating regime change. In the cooling curve, the sample begins to gain mass at the phase transition temperature (labelled D). After thermal cycling the sample had changed colour from yellow to dark green, consistent with Ce oxidation as described in section 3.1.

3.4 Electrochemical Impedance Spectroscopy (EIS)

Two samples were compared by EIS: (i) a sintered pellet of CeNbO_{4+δ} powder prepared in air and (ii) the single crystal of CeNbO₄ prepared in argon. Polycrystalline powders, of the same composition as single crystals will exhibit lower oxygen mobility compared to single crystals due to the high impedance of grain boundaries. Non-stoichiometric CeNbO_{4+δ} compounds ($\delta \neq 0$) should be superior ion conductors, with lower activation energies than the stoichiometric material. The present experiments found that at low temperatures (150-200°C) the total conductivity of the extra-stoichiometric sintered pellet and stoichiometric single crystal samples are comparable (Figure 10). However, at 600°C the performance of the sintered pellet containing interstitial oxygen (activation energy = 0.46 eV, $\sim 10^{-2}$ S/cm) exceeds the single crystal (activation energy = 0.36 eV, $\sim 10^{-3}$ S/cm). The activation energies of ionic conductors are typically of the order of ≈ 1 eV, and the lower values here suggest the possibility of mixed conductivity in these samples. EIS of the CeNbO₄ single crystal was performed in argon to limit Ce^{3+/4+} oxidation, whilst EIS of the sintered pellet to create oxygen superstoichiometry ($\delta \neq 0$), and responses were separated into bulk and grain boundary components [26]. These measurements show that oxygen incorporation into the CeNbO_{4+δ} enhances conductivity, and that stoichiometric CeNbO₄ has poor transport properties.

4. Conclusions

In summary, the growth of single crystals has permitted the most precise structural analysis of stoichiometric CeNbO_4 performed to date. Powder diffraction showed single phase CeNbO_4 was only obtained by growth in argon, whilst the synthesis in air yielded $\text{CeNbO}_{4.08}$ as a minor phase. For argon derived material, the high crystal quality was confirmed via rocking curve analysis. Direct methods established that CeNbO_4 conformed to the $C12/c1$ standard setting, which was transformed to $I12/a1$, for comparison with the high temperature scheelite-type polymorph. It is noted that the literature contains several instances of incorrect use of $I12/a1$ pseudo-tetragonal setting, and the correct lattice parameters have $a = 5.1621(4)$ Å, $b = 11.4030(5)$ Å, $c = 5.5365(2)$ Å and $\beta = 94.594(11)^\circ$, and not as previously reported, with the a and c lattice parameters reversed. AC impedance spectroscopy of the CeNbO_4 single crystal performed under argon as a function of temperature suppressed oxidation and was compared to a sintered polycrystalline ceramic $\text{CeNbO}_{4+\delta}$ containing excess interstitial oxygen measured in air. These materials are found to have distinct activation energies at 600°C (0.36eV for $\text{CeNbO}_{4+\delta}$ / 0.46eV for CeNbO_4) and in $\text{CeNbO}_{4+\delta}$ oxygen migration is an order of magnitude higher. From a fuel cell application perspective the TGA/DSC experiments demonstrate that at temperatures $> 730^\circ\text{C}$ the $\text{CeNbO}_{4+\delta}$ expels all the interstitial oxygen to become stoichiometric CeNbO_4 . The absence of the O^{2-} charge carriers in this high temperature regime would severely degrade its performance in a solid-oxide fuel cell.

Acknowledgments

The authors thank the Royal Academy of Engineering and Imperial College London for travel funding for RDB, and the EPSRC for funding the studentship for RDB. We acknowledge the Singapore Ministry of Education (MOE) Tier 2 grant number T208B1212 for funding the single crystal diffractometer and A*STAR PSF grant number 082 101 0021 for the optical floating zone furnace.

Figures and Tables

Figure 1. Photograph of the as grown single crystal of CeNbO_4 prepared in argon gas. Each square represents 1mm^2 . The yellow portion on the right side of the crystal is a section of the polycrystalline feed rod.

Figure 2. Comparison of the powder X-ray diffraction patterns of the air and argon grown crystals. The arrows indicate the weak reflections tentatively assigned as the minor impurity phase $\text{CeNbO}_{4.08}$ identified in reference [7].

Figure 3. Rietveld refinement of the powder X-ray diffraction pattern of the single crystal CeNbO_4 prepared in flowing argon gas. The model determined from the single crystal study was used for the refinement with only instrumental parameters refined.

Figure 4. Direct cell symmetry relationship between the $I12/a1$ and $C12/c1$ for CeNbO_4 .

Figure 5. A polyhedral representation of NbO_4 tetrahedra highlighting the structural relationships between the tetragonal ($I4_1/a$) scheelite-type structure and the I and C centred monoclinic cells for CeNbO_4 .

Figure 6. Three dimensional difference Fourier map indicating regions of excess electron density $> 2 \text{ e}/\text{\AA}^3$, which are close to the Ce^{3+} and Nb^{5+} positions, and possibly a consequence of a non-ideal absorption correction. The yellow, green and red spheres represent the Ce, Nb and O ions respectively.

Figure 7. Rocking curve analysis of the as grown single crystal of CeNbO_4 prepared in argon gas. Analysis performed on the (041) reflection showing a FWHM of 0.18° reflects the high quality of the crystal sample.

Figure 8. [a] A high resolution transmission electron microscopy (HRTEM) image of CeNbO_4 , which shows a periodic crystal with thickness fringes. [b] Selected area electron diffraction (SAED) pattern of CeNbO_4 [101] indexed in the spacegroup $C12/c1$ with no evidence of super-structure reflections.

Figure 9. TGA/DSC profile for CeNbO_4 heated to 1000°C in air and cooled to room temperature. The arrows from left to right (A, B, D) represent key changes in crystal structure and redox chemistry processes (C is an instrumental artefact caused by a change in the heating regime).

Figure 10. Arrhenius plot showing total conductivity ($\log \sigma$) as a function of temperature of both $\text{CeNbO}_{4+\delta}$ sintered pellets of powders (black squares) performed in air and a section of single crystal CeNbO_4 (red circles) performed under argon to prevent oxidation.

Table 1. Refined atomic parameters from single crystal X-ray diffraction of CeNbO_4 refined in the space group setting $C12/c$. Final statistical values for quality of fit were $R = 0.0258$; $wR = 0.0737$; $\text{GoF} = 2.31$

S.G.	$C12/c1$	$a = 7.2609(3) \text{ \AA}$	$b = 11.4032(4) \text{ \AA}$	$c = 5.1621(2) \text{ \AA}$	$\beta = 130.530(1)^\circ$
Site	Wyckoff	x	y	z	U_{Iso}
Ce	$4e$	0	0.62963(5)	1/4	0.0045(2)
Nb	$4e$	0	0.10286(13)	1/4	0.0040(2)
O(1)	$8f$	0.2635(4)	0.4669(2)	0.3109(6)	0.0084(11)
O(2)	$8f$	0.1484(4)	0.2050(2)	0.1583(6)	0.0071(10)

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce	0.00463(18)	0.0051(2)	0.0047(2)	0	0.0033(1)	0
Nb	0.0046(2)	0.0058(3)	0.0025(2)	0	0.0026(1)	0
O(1)	0.0083(9)	0.007(1)	0.0084(10)	0.0009(8)	0.0050(8)	-0.0005(8)
O(2)	0.0079(9)	0.0051(9)	0.0109(11)	0.0005(8)	0.0072(8)	0.0016(8)

Crystal size	$0.08 \times 0.1 \times 0.1 \text{ mm}$
--------------	---

Crystal system	Monoclinic
Space group	$C12/c1$ (No. 15)
Unit cell dimensions	
a (Å)	7.2609(3)
b (Å)	11.4032(4)
c (Å)	5.1621(2)
β (°)	130.5301(11)
V (Å ³)	324.86(2)
Z	4
Density (g cm ⁻³)	6.071
μ (cm ⁻¹)	17.189
Radiation Mo $K\alpha$ (Å)	0.71073
Collection limits (θ , deg)	3.57 – 34.22
Range of h, k, l	-11 $\rightarrow$ h $\rightarrow$ 12 -18 $\rightarrow$ k $\rightarrow$ 17 -8 $\rightarrow$ l $\rightarrow$ 8
Data measured	3251
Unique reflections	740
Reflections with $I \geq 3\sigma(I)$	
R	0.0258
R_w	0.0737
GOF	2.31
D residual (eÅ ⁻³)	
+	4.73
-	-1.99

Table 2. Selected bond distances derived from single crystal X-ray diffraction

Cerium Polyhedron	Å	Niobium Polyhedron	Å
Ce – O(1) $\times$ 2	2.461(2)	Nb – O(1) $\times$ 2	1.914(2)
Ce – O(1) $\times$ 2	2.534(3)	Nb – O(2) $\times$ 2	1.845(3)
Ce – O(2) $\times$ 2	2.431(3)	Nb – O(1) $\times$ 2	2.480(3)
Ce – O(2) $\times$ 2	2.491(3)		
Average	2.479	Average	2.079

Table 3. Equivalent parameters for CeNbO₄ in the space group $I12/a1$. Transformation from $I12/a1$ to $C12/c1$ (-a-c, b, a) origin $\frac{1}{4} \frac{1}{4} \frac{1}{2}$.

S.G.	$I12/a1$	$a = 5.1621(4)$ Å	$b = 11.4032(5)$ Å	$c = 5.5365(2)$ Å	$\beta = 94.594(1)$ Å
Site	Wyckoff	x	y	z	U_{Iso}
Ce	4e	0.75	0.12953(3)	0.5	0.00489(15)
Nb	4e	0.25	0.10278(6)	0	0.00434(17)
O(1)	8f	0.0470(5)	0.0330(3)	0.2366(4)	0.0085(7)
O(2)	8f	0.4899(5)	0.2051(2)	0.1482(5)	0.0071(7)

References

- [1] J.B. Goodenough, *Annu. Rev. Mater. Res.* 33 (2003) 91.
- [2] A. Orera, P.R. Slater, *Chem. Mater.* 22 (2010) 675-690.
- [3] X. Kuang, M.A. Green, H. Niu, P. Zajdel, C. Dickinson, J.B. Claridge, L. Jantsky, M.J. Rosseinsky, *Nat. Mater.* 7 (2008) 498-504.
- [4] M.C. Martín-Sedeño, E.R. Losilla, L. León-Reina, S. Bruque, D. Marrero-López, P. Núñez, M.A.G. Aranda, *Chem. Mater.* 16 (2004) 4960-4968.
- [5] S.J. Skinner, J.A. Kilner, *Solid State Ionics* 135 (2000) 709-712.
- [6] R.J. Packer, S.J. Skinner, *Adv. Mater.* 22 (2010) 1613-1616.
- [7] J.G. Thompson, R.L. Withers, F.J. Brink, *J. Solid State Chem.* 143 (1999) 122-131.
- [8] S.J. Skinner, Y. Kang, *Solid State Sci.* 5 (2003) 1475-1479.
- [9] A. Santoro, M. Marezio, R.S. Roth, D. Minor, *J. Solid State Chem.* 35 (1980) 167-175.
- [10] S.J. Skinner, I.J.E. Brooks, C.N. Munnings, *Acta. Crystallogr. C* 60 (2004) i37-i39.
- [11] E.V. Tsipis, C.N. Munnings, V.V. Kharton, S.J. Skinner, J.R. Frade, *Solid State Ionics* 177 (2006) 1015-1020.
- [12] R.J. Packer, E.V. Tsipis, C.N. Munnings, V.V. Kharton, S.J. Skinner, J.R. Frade, *Solid State Ionics* 177 (2006) 2059-2064.
- [13] S.J. Skinner, R.J. Packer, R.D. Bayliss, B. Illy, C. Prestipino, M.P. Ryan, *Solid State Ionics* 192 (2011) 659-663.
- [14] R. Guo, Y. Jiang, A.S. Bhalla, L.E. Cross, Applications of Ferroelectrics, 1996. ISAF'96., Proceedings of the Tenth IEEE International Symposium on, East Brunswick, NJ, 1996, pp. 899-902.
- [15] F. Vullum, F. Nitsche, S.M. Selbach, T. Grande, *J. Solid State Chem.* 181 (2008) 2580-2585.
- [16] Inorganic Crystal Structure Database, Version 2010-2, Fiz-Karlsruhe, Germany.
- [17] R.W. Cheary, A. Coelho, *J. Appl. Crystallogr.* 25 (1992) 109-121.
- [18] R.W. Cheary, A. Coelho, *J. Appl. Crystallogr.* 31 (1998) 851-861.
- [19] V. Petříček, M. Dusek, L. Palatinus, Institute of Physics, Praha, Czech Republic, 2006.
- [20] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* 40 (2007) 786-790.
- [21] K. Momma, F. Izumi, *J. Appl. Cryst.* 41 (2008) 653-658.
- [22] A.R. West, D.C. Sinclair, *J. Electroceramics* 1 (1997) 65-71.
- [23] V.K. Trunov, V.A. Efremov, Y.A. Velikodnyi, I.M. Averina, *Kristallografiya* 26 (1981) 67-71.
- [24] M. Machida, J. Kido, T. Kobayashi, S. Fukui, N. Koyano, Y. Suemune, *Kyoto University, Research Reactor Institute: Annual Report* 28 (1995) 25-32.
- [25] T. An, T. Baikie, F. Wei, H. Li, F. Brink, J. Wei, S.L. Ngoh, T.J. White, C. Kloc, *J. Cryst. Growth* 333 (2011) 70-73.
- [26] R.J. Packer, Department of Materials, Imperial College London, 2010.