# Tetragonal CeNbO$_4$ at 1073 K in air and *in vacuo*

**Stephen J. Skinner,\* Ian J. E. Brooks and Christopher N. Munnings**

Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, England
Correspondence e-mail: s.skinner@imperial.ac.uk

The structure of the high-temperature scheelite-type polymorph of cerium niobium tetraoxide, CeNbO$_4$, has been determined using time-of-flight neutron powder diffraction data collected both *in situ* at 1073 K in air and *in vacuo*. In both cases, the structure was found to be tetragonal, with $I4_1/a$ symmetry and without any significant deviation from the stoichiometric composition.

## Comment

Several authors have investigated the structure of CeNbO$_4$, particularly under ambient conditions (Negas *et al.*, 1977; Roth *et al.*, 1977, 1978; Cava *et al.*, 1978; Santoro *et al.*, 1980; Thompson *et al.*, 1999), and only recently has there been any attempt to characterize the structure at elevated temperatures, with one recent report of an *in situ* characterization of phase transformations on heating that presented minimal structural information (Skinner & Kang, 2003). The recent interest in this material has stemmed from the possible incorporation of oxygen interstitials that would make this material amenable to oxide ion conducting applications, such as solid electrolytes, sensors and separation membranes. The purpose of this study was to investigate the structure of the high-temperature polymorph under both static air and vacuum conditions in order to gather information regarding the likely flexibility of oxygen stoichiometry in CeNbO$_4$.

The low-temperature polymorph of CeNbO$_4$ has been described previously as a monoclinic distortion of the tetragonal scheelite structure, adopting a fergusonite-type structure (Santoro *et al.*, 1980; Thompson *et al.*, 1999). It was also predicted that CeNbO$_4$ will undergo oxidation on heating in air and a structural transition on heating above 847 K (Gingerich & Blair, 1964; Negas *et al.*, 1977; Roth *et al.*, 1977; Cava *et al.*, 1978). Recently, *in situ* measurements have raised questions about the nature of these oxidation and transformation processes (Skinner & Kang, 2003). However, until the present work, there has been no determination of the structure of the tetragonal form of CeNbO$_4$. From our initial X-ray

diffraction results, it was immediately apparent that the data recorded at 1073 K conformed to a scheelite-type structure. As a starting model for the Rietveld refinement of the neutron powder diffraction data, the structure of scheelite (CaWO$_4$) was therefore used [space group $I4_1/a$; alternate setting with origin at $(0, \frac{1}{4}, \frac{1}{8})$; the Ce and Nb atoms in the $4b$ and $4a$ positions, respectively, and the O atom in the $16f$ position (Hazen *et al.*, 1985)]. The refinements were carried out using the *GSAS* package (Larson & Von Dreele, 1994) and provided good fits to the 90° and backscattered neutron diffraction data collected in air and *in vacuo* ($10^{-3}$ Pa) (Fig. 1).

In common with other scheelite-type compounds, the Ce atoms in CeNbO$_4$ are in an eightfold coordination environment, with two distinct bond lengths, while the Nb environment is tetrahedral, with equal Nb—O bonds (Fig. 2). The slightly larger unit-cell volume of the sample heated in static
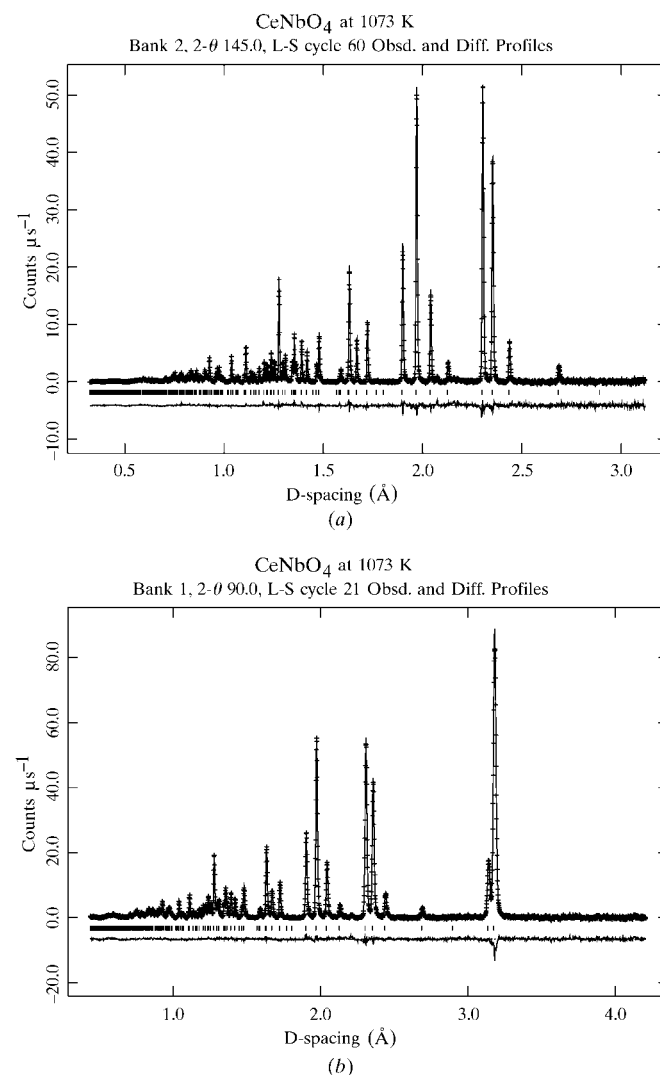


**Figure 1**
(*a*) A Rietveld plot for the refinement of backscattered neutron diffraction data *in vacuo*. The experimental and calculated profiles are represented by crosses and a full line, respectively. The difference plot is shown underneath and tick marks indicate the positions of Bragg reflections. (*b*) A Rietveld plot for the refinement of the 90° bank neutron diffraction data in air. Profiles are drawn as in (*a*).

# inorganic compounds
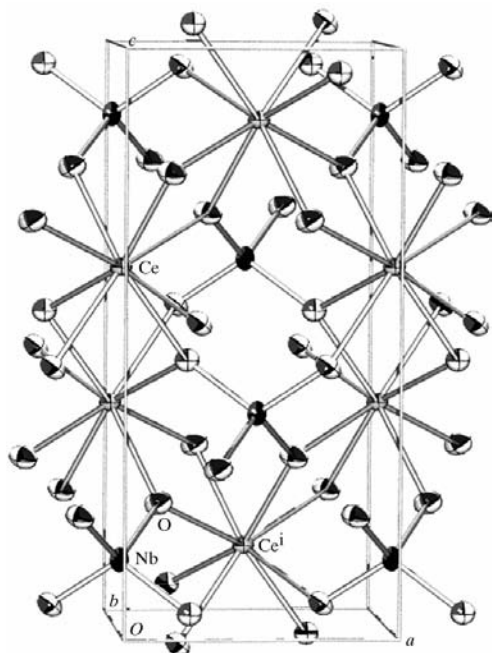


**Figure 2**
A representation of the tetragonal scheelite-type structure of CeNbO$_4$, showing the Nb and Ce coordination environments. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2} - z$.]

air is associated with slightly longer Nb—O and Ce—O distances (Tables 1 and 2). The distorted tetrahedral environment for the Nb atom, with O—Nb—O angles of 106.476 (19) and 115.64 (4)°, is comparable to that in isostructural LaNbO$_4$ (David, 1983; Machida *et al.*, 1995). The transition temperature in CeNbO$_4$ is significantly higher than that in LaNbO$_4$ (773 K).

From the results of both refinements and from Fourier difference maps, it is apparent that the high-temperature CeNbO$_4$ polymorph is fully stoichiometric, and there is no evidence to suggest that heating it in air introduced any interstitial oxygen. Because the sample was heated *in situ* while packed in a vanadium can, it is conceivable that limited oxidation occurred at the surface only. Hence, it would be desirable either to perform a series of measurements at one temperature over a period of time to enable the study of possible oxygen incorporation into CeNbO$_4$ or to oxidize a sample before carrying out a set of measurements at temperatures up to 1073 K, allowing any oxygen stoichiometry variations on heating to be investigated.

## Experimental

Samples were produced through the mixing of CeO$_2$ (99.9%, Sigma Aldrich) and Nb$_2$O$_5$ (99.99%, Sigma Aldrich) in an agate mortar and pestle. These starting materials were mixed thoroughly under acetone and allowed to dry in air before the stoichiometric mixture was transferred to an alumina crucible for heat treatment. The mixture was prefired at 1273 K for 10 h and allowed to cool. After further mixing, the material was heated at 1673 K for 16 h and quenched.

This procedure produced a bright-green material. X-ray powder diffraction data were recorded on a Philips PW1700 series diffractometer using Cu $K\alpha_1$ radiation and a graphite crystal as secondary monochromator. Neutron powder diffraction data were collected from 6 g samples contained in vanadium cans on the POLARIS diffractometer using both 90° and backscatter detectors at ISIS, CCLRC Rutherford Appleton Laboratory, Oxfordshire, England. Each data set was collected over a period of 90 min, and then normalized and corrected in the usual way. Two separate samples were examined during these measurements. The first sample was heated *in situ* under vacuum with data recorded on heating and cooling. For the second sample, the same *in situ* heating regime was used but the can was exposed to static air. The data were collected at 296 K, every 100 K from 473 to 973 K, and every 50 K from 973 to 1123 K. On cooling, data were recorded at 1023, 823 and 623 K. Only the data recorded at 1073 K from the samples heated in air and *in vacuo* are included here.

### In vacuo

*Crystal data*

| | |
|---|---|
| CeNbO$_4$ | $Z = 4$ |
| $M_r = 297.02$ | $D_x = 5.905$ Mg m$^{-3}$ |
| Tetragonal, $I4_1/a$, origin choice 2 at $(0, \frac{1}{4}, \frac{1}{8})$ from $\overline{4}$ | Neutron radiation |
| | $\lambda = 0.1$–6.0 Å |
| $a = 5.37119$ (8) Å | $T = 1073$ K |
| $c = 11.58104$ (18) Å | Light green |
| $V = 334.109$ (9) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Polaris diffractometer at ISIS (England) | Specimen mounting: 6 mm diameter vanadium can |
| | 2884 independent reflections |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Profile function: exponential pseudo-Voigt convolution |
| $R_p = 0.0196$ | |
| $R_{wp} = 0.0116$ | 2884 reflections |
| $R_{exp} = 0.0065$ | 49 parameters |
| $S = 1.81$ | $(\Delta/\sigma)_{max} = 0.02$ |

**Table 1**
Selected interatomic distances (Å) for vacuum data.

| Ce$\cdots$Ce | 3.94904 (4) | Ce—O$^{iii}$ | 2.4847 (6) |
|---|---|---|---|
| Ce—O$^{ii}$ | 2.5100 (6) | Nb—O | 1.8537 (5) |

Symmetry codes: (ii) $-x, 1 - y, 1 - z$; (iii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$.

### In air

*Crystal data*

| | |
|---|---|
| CeNbO$_4$ | $Z = 4$ |
| $M_r = 297.02$ | $D_x = 5.835$ Mg m$^{-3}$ |
| Tetragonal, $I4_1/a$, origin choice 2 at $(0, \frac{1}{4}, \frac{1}{8})$ from $\overline{4}$ | Neutron radiation |
| | $\lambda = 0.1$–6.0 Å |
| $a = 5.37692$ (8) Å | $T = 1073$ K |
| $c = 11.59514$ (18) Å | Light green |
| $V = 335.230$ (8) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Polaris diffractometer at ISIS (England) | Specimen mounting: 6 mm diameter vanadium can |
| | 2884 independent reflections |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Profile function: exponential |
| $R_p$ = 0.0203 | pseudo-Voigt convolution |
| $R_{wp}$ = 0.0118 | 2884 reflections |
| $R_{exp}$ = 0.0065 | 49 parameters |
| $S$ = 1.83 | $(\Delta/\sigma)_{max}$ = 0.03 |

**Table 2**
Selected interatomic distances (Å) for air data.

| | | | |
|---|---|---|---|
| Ce···Ce$^{iv}$ | 3.95358 (4) | Ce—O$^{iii}$ | 2.4882 (6) |
| Ce—O$^{ii}$ | 2.5128 (6) | Nb—O | 1.8553 (5) |

Symmetry codes: (ii) $-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (iv) $-\frac{1}{4}-y, \frac{1}{4}+x, \frac{1}{4}+z$.

Initial refinement cycles showed no significant deviation from stoichiometry, and therefore the occupancies of the Ce- and Nb-atom sites were fixed to unity in the final cycles for both the air and the vacuum data sets. The occupancy of the O-atom site was allowed to vary but did not deviate significantly from unity either. Fourier difference maps indicated no significant residual scattering density within the unit cell, with maxima of 0.49 Å$^{-3}$ at (0.2465, 0.5004, 0.1234) for the vacuum data and 0.46 Å$^{-3}$ at (0.1545, 0.9652, 0.1803) for the air data.

For both compounds, data collection: Polaris instrument control program; cell refinement: *GSAS* (Larson & Von Dreele, 1994); program(s) used to solve structure: *GSAS*; program(s) used to refine structure: *GSAS*; molecular graphics: *GRETEP* (Laugier & Bochu, 2004) and *POVRAY* (URL: www.povray.org).

## References

Cava, R. J., Negas, T., Roth, R. S., Parker, H. S., Minor, D. B. & Olson, C. D. (1978). *The Rare Earths in Modern Science and Technology*, edited by G. J. McCarthy & J. J. Rhyne, pp. 181–187. New York/London: Plenum Press.

David, W. I. F. (1983). *Mater. Res. Bull.* **18**, 749–756.

Gingerich, K. A. & Blair, H. E. (1964). *Adv. X-ray Anal.* **7**, 22–30.

Hazen, R. M., Finger, L. W. & Mariathasan, J. W. E. (1985). *J. Phys. Chem. Solids*, **46**, 253–263.

Larson, A. C. & Von Dreele, R. B. (1994). *GSAS.* Report No. LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.

Laugier, J. & Bochu, B., (2004). *GRETEP.* LMPG, Grenoble, France.

Machida, M., Kido, J., Kobagashi, T., Fukui, S., Koyano, N. & Suemone, Y. (1995). Annual Reports 25–32. Kyoto University Research Reactor Institute, Japan.

Negas, T., Roth, R. S., McDaniel, C. L., Parker, H. S. & Olson, C. D. (1977). *Mater. Res. Bull.* **12**, 1161–1172.

Roth, R. S., Negas, T., Parker, H. S., Minor, D. B. & Jones, C. (1977). *Mater. Res. Bull.* **12**, 1173–1182.

Roth, R. S., Negas, T., Parker, H. S., Minor, D. B., Olson, C. D. & Skarda, C. (1978). *The Rare Earths in Modern Science and Technology*, edited by G. J. McCarthy & J. J. Rhyne, pp. 163–171. New York/London: Plenum Press.

Santoro, A., Marezio, M., Roth, R. S. & Minor, D. (1980). *J. Solid State Chem.* **35**, 167–175.

Skinner, S. J. & Kang, Y. (2003). *Solid State Sci.* **5**, 1475–1479.

Thompson, J. G., Withers, R. L. & Brink, F. J. (1999). *J. Solid State Chem.* **143**, 122–131.