Oxidation Driven Decomposition of $CeNbO_4$ in Pure Oxygen

Fride Vullum and Tor Grande*

Department of Materials Science and Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway

Received April 30, 2008. Revised Manuscript Received June 9, 2008

$CeNbO_4$ possesses oxygen hyper-stoichiometry at ambient and moderate temperature. At elevated temperature $CeNbO_{4+\delta}$ is thermally reduced to near stoichiometric $CeNbO_4$ accompanied by a structural phase transition. Above the phase transition temperature reoxidation of the material occurred in a pure oxygen atmosphere, and in situ X-ray diffraction revealed that $CeNbO_4$ decomposed to CeO_2 and $CeNb_3O_9$. Upon further heating $CeNbO_4$ reappeared by a solid state reaction between CeO_2 and $CeNb_3O_9$. The present findings demonstrate that $CeNbO_{4+\delta}$ is metastable with respect to CeO_2 and $CeNb_3O_9$ at low temperature.

Introduction

The crystal structure of $CeNbO_4$ is already well-known and can be identified as a monoclinic Fergusonite-type structure at room temperature, transforming to a tetragonal Scheelite-type structure at 574 °C in vacuum.[1,2] Cooling $CeNbO_4$ in an oxidizing atmosphere results in hyper-stoichiometric $CeNbO_{4+\delta}$, and several crystal structures with specific oxygen stoichiometry have been reported (i.e., $CeNbO_{4.08}$, $CeNbO_{4.25}$, and $CeNbO_{4.33}$).[1,2] The defect chemistry and transport properties of $CeNbO_{4+\delta}$ have been investigated, and the material is found to possess mixed electronic and ionic conductivity at elevated temperature due to the mixed valence state of Ce and interstitial oxygen anions.[3–5] Applications of ceramic materials in fuel cells or oxygen permeable membranes require high material stability, and the stability of mixed conducting materials may be challenged at low oxygen partial pressure where decomposition of the material may occur due to reduction. Here, we report the on decomposition of $CeNbO_{4+\delta}$ caused by oxidation in pure oxygen atmosphere. Decomposition due to oxidation upon heating is a rare phenomenon in solid state chemistry.

Experimental Section

$CeNbO_{4+\delta}$ was prepared by spray pyrolysis as described by Vullum and Grande.[5] Aqueous solutions of 0.2 M Ce−citric acid complex and 0.16 M Nb−malic acid complex were prepared. The Nb−malic acid complex solution was prepared from 0.78 mol of $(NH_4)NbO(C_2O_4)_2\cdot 5H_2O$ (H. C. Starck) and DL-malic acid (0.33 M) (Aldrich, 99%) by the method described by Mokkelbost et al.[6] The Ce−citric acid complex solution was prepared by dissolving 1.0 mol of cerium nitrate ($Ce(NO_3)_3\cdot 6H_2O$, Alfa Aesar, 99.5%) in approximately 3 L of distilled water and mixing with 1.3 mol citric acid ($C_6H_8O_7$, Acros Organics). Ammonium hydroxide (25%) was added to the solution to form the water-soluble Ce−citric acid complex. pH was adjusted to 8.5 by dropwise addition of 65% nitric acid (HNO_3). The cation content in the Ce−citric acid and the Nb−malic acid solutions was determined by thermogravimetry (weight of oxide after thermal treatment) and mixed to give the desired stoichiometry. Prior to mixing it was imperative that the solutions were adjusted to pH 8.5 in order to avoid precipitation during mixing. The homogeneous solution was processed using pilot scale spray pyrolysis equipment.[6] The raw powder produced from the pyrolysis was first dry ball milled for 20−30 min in order to reduce the tap density, followed by calcination at 800 °C in air for 6 h, and finally wet ball milled in 100% ethanol for approximately 24 h. Powder used for thermal analysis was heated at 1200 °C for 50 h in air prior to the analysis.

Thermogravimetric analysis (TGA) of the powder was performed using a Netzsch STA 449C instrument in atmospheres of 0.008 bar, 0.2 bar, and 1 bar oxygen partial pressure. The heating and cooling rates were 2 °C/min, and 2 h isothermal holds were performed at 800, 850, 900, 1000, and 1100 °C on heating and 1000, 900, and 800 °C on cooling. In addition, dilatometry was performed on dense pellets in both 0.2 and 1 bar oxygen partial pressure using a Netzsch DIL 402C. The pellets were cold pressed from calcined and ball milled pyrolysis powder followed by sintering at 1200 °C in order to achieve a density of approximately 98% of theoretical density. The sintered pellet was heated and cooled at 2 °C/min with a 2 h isothermal hold at a maximum temperature of 1100 °C.

Qualitative powder X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance diffractometer with Våntec detector and Cu Kα radiation. High temperature X-ray diffraction (HTXRD) was performed in both air and pure oxygen using a Siemens D5005 $\theta-\theta$ diffractometer with Cu Kα radiation, a secondary monochromator and a HTK 16 Anton Paar GMbh high temperature camera. The temperature of the high temperature

---

* To whom correspondence should be addressed. E-mail: tor.grande@material.ntnu.no.

(1) Thompson, J. G.; Withers, R. L.; Brink, F. *J. Solid State Chem.* **1999**, *143*, 122.
(2) Skinner, S. J.; Kang, Y. *Solid State Sci.* **2003**, *5*, 1475.
(3) Tsipis, E. V.; Munnings, C. N.; Kharton, V. V.; Skinner, S. J.; Frade, J. R. *Solid State Ionics* **2006**, *177*, 1015.
(4) Packer, R. J; Tsipis, E. V; Munnings, C. N; Kharton, V. V.; Skinner, S. J; Frade, J. R. *Solid State Ionics* **2006**, *177*, 2059.
(5) Vullum, F; Grande, T. Oxygen Stoichiometry and Transport Properties of Cerium Niobate. *Solid State Ionics* **2008**, DOI: 10.1016/j.ssi.2007.12.079.
(6) Mokkelbost, T.; Andersen, Ø.; Strøm, R. A.; Wiik, K.; Grande, T.; Einarsrud, M.-A. *J. Am. Ceram. Soc.* **2007**, *90*, 3395.

10.1021/cm801178a CCC: $40.75

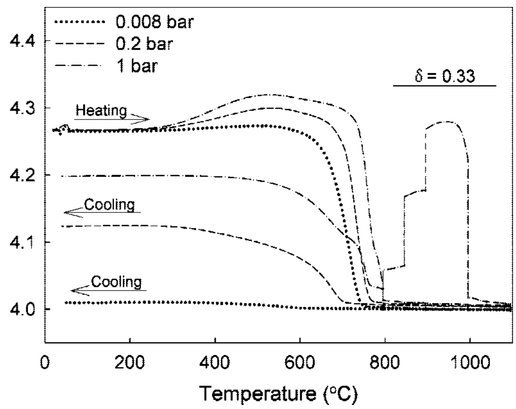

Figure 1. TGA of $CeNbO_{4+\delta}$ powder at three different oxygen partial pressures.

camera has been calibrated by refinement of the diffraction data from the Pt heating element at various temperatures.

Results and Discussion

Powder calcined in air at 800 °C and cooled to ambient temperature was shown by X-ray diffraction to contain two $CeNbO_{4+\delta}$ phases with different oxygen contents and crystal structures in accordance with previous reports.[1,2] The oxygen hyper-stoichiometry of the powders during heating and cooling was investigated by TGA, and the results are shown in Figure 1. The weight changes during isothermal annealing for 2 h were monitored at 800, 850, 900, 1000, and 1100 °C on heating and at 1000, 900, and 800 °C on cooling. During heating the material goes through a phase transition from monoclinic $CeNbO_{4+\delta}$ to tetragonal $CeNbO_{4+\delta}$ in the temperature range 700−800 °C.[1,2,5,7] The phase transition is associated with a significant weight loss due to reduction of Ce(IV) to Ce(III) resulting in a change in the oxygen hyper-stoichiometry from $\delta \sim 0.32$ to a near stoichiometric $CeNbO_4$. The phase transition temperature, defined as the thermal onset of the rapid reduction in oxygen content, is clearly decreasing with reduction in the partial pressure of oxygen. This can be illustrated by the simplified chemical reaction

$$\text{m-}CeNbO_{4+\delta} \rightleftharpoons \text{t-}CeNbO_4 + \delta/2O_2(g) \qquad (1)$$

when neglecting the small oxygen hyper-stoichiometry for the tetragonal phase. By lowering the partial pressure of oxygen the phase transition temperature is shifted to lower temperatures in line with the results shown in Figure 1.

Upon further heating in 0.2 (air) or 0.008 bar pO_2 only minor reduction of the oxygen hyper-stoichiometry is observed, as we have reported previously.[5] When the powder is cooled from 1100 °C in these two partial pressures of oxygen the material is reoxidized, but considerable hysteresis of the phase transition is observed, revealing its first order nature. Moreover, the resulting oxygen hyper-stoichiometry after cooling to ambient temperature is considerably lower than the initial oxygen content in the powders, demonstrating that the rate of oxidation of $CeNbO_4$ is slow.

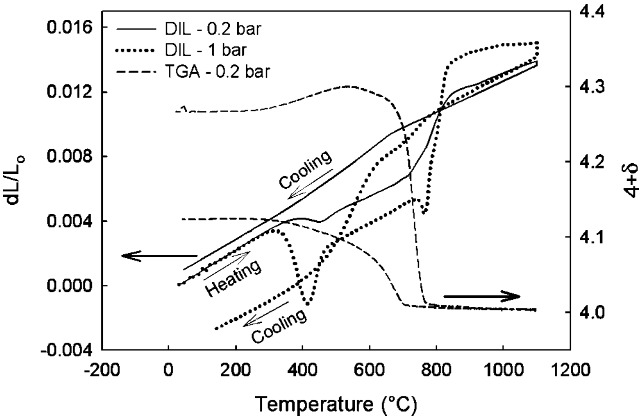

Figure 2. Dilatometer curves in 0.2 and 1 bar oxygen partial pressure combined with TGA data at 0.2 bar.

Contrary to the expectations, in pure oxygen atmosphere (1 bar) the material immediately started to gain mass after the reduction due to reaction 1. The increase in oxygen content was observed to start during the isothermal hold at 800 °C, to continue during heating and isothermal hold at 850 and 900 °C, and to reach a maximum oxygen content corresponding to $\delta \sim 0.28$ near 950 °C. Upon further heating a second reduction was initiated and resulted in a significant weight loss during the isothermal hold at 1000 °C. Oxidation during heating was highly unexpected, and the reoxidation and reduction of the sample after completion of reaction 1 was reproduced several times in order to prove that this was not an experimental artifact.

Complementary dilatometry measurements on dense polycrystalline $CeNbO_4$ were also performed. Figure 2 gives the dilatometry curves at 0.2 and 1 bar oxygen partial pressure. The TGA curve at 0.2 bar is included in the figure in order to better compare the absorption of oxygen at specific temperatures with the expansion of the sample. The dilatometry curve obtained at 0.2 bar O_2 clearly shows that the material shrinks upon heating in a certain temperature range, demonstrating that the material is oxidized, leading to a shrinkage of the ionic radii of cerium. Upon further heating the sample again starts to expand due to the reduction around the phase transition temperature. During cooling the oxidation process is much slower and the sample shrinks, although not in a completely linear fashion, more according to what is expected for a ceramic material. The curve collected in pure oxygen atmosphere is similar to what is seen at 0.2 bar, except the sample experiences a larger extent of shrinkage due to higher degree of oxidation and more Ce changing from Ce(III) to Ce(IV). It is important to note that the oxidation driven decomposition of $CeNbO_4$, clearly observed for powder samples by TGA, was not observed for the dense ceramic samples as might be expected based on slower kinetics for dense materials.

Oxidation of a material during heating is not expected to occur at equilibrium conditions, and high temperature X-ray diffraction was performed in order to understand the nature of the oxidation process observed to initiate at 800 °C. The HTXRD data of the $CeNbO_{4+\delta}$ powder in air and in pure oxygen are shown in Figure 3a,b. In air the diffraction

---

(7) Skinner, S. J.; Brooks, I. J. E.; Munnings, C. N. *Acta Crystallogr.* **2004**, *C60*, i37.

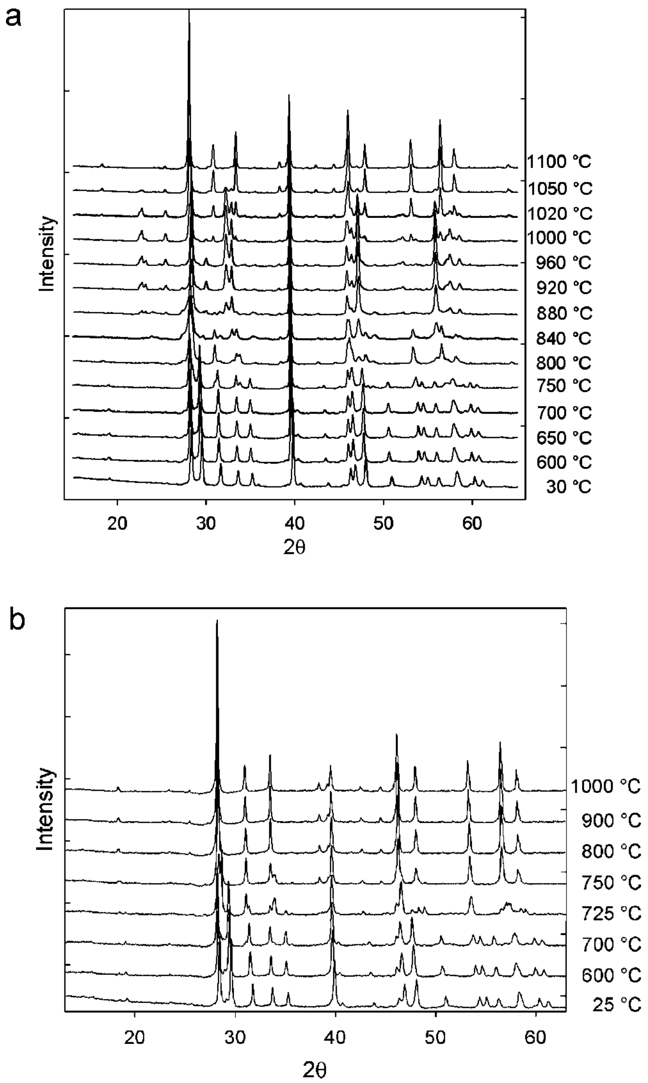

Figure 3. a: High temperature XRD data for $CeNbO_{4+\delta}$ in pure O_2 atmosphere. b: High temperature XRD data for $CeNbO_{4+\delta}$ in air.

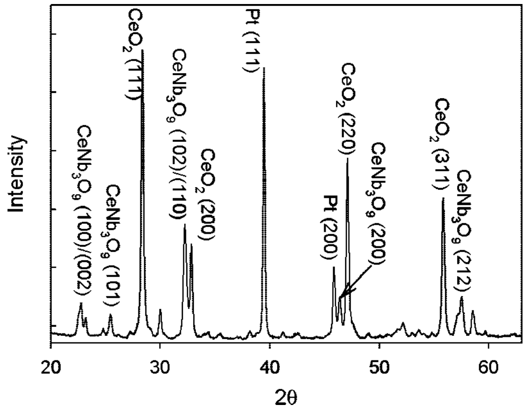

Figure 4. High temperature XRD data at 960 °C demonstrating the presence of CeO_2 and $CeNb_3O_9$.

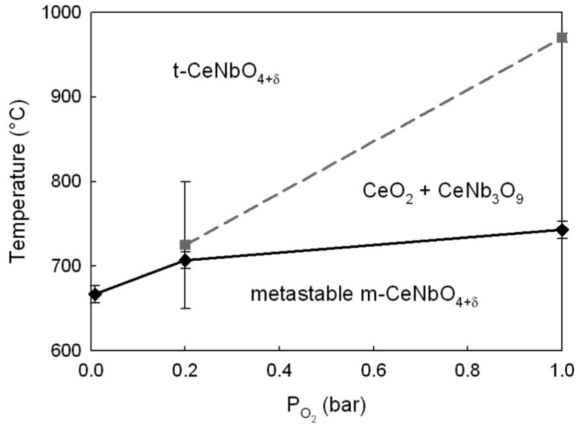

Figure 5. Decomposition temperature of $CeNbO_{4+\delta}$ to CeO_2 and $CeNb_3O_9$ and the monoclinic to tetragonal phase transition temperature of $CeNbO_{4+\delta}$ as a function of partial pressure of oxygen.

patterns observed below the phase transition 1 could be indexed to monoclinic $CeNbO_{4+\delta}$ (JCPDS 33-0332), while above the transition the diffraction patterns are in accordance with tetragonal $CeNbO_{4+\delta}$.[2] The diffractograms recorded in pure oxygen are relatively similar to the ones obtain in air up to 800 °C, while the diffraction patterns recorded at 840, 880, 920 and 960 °C in pure oxygen contained several reflections which could not be indexed to any known polymorphs of $CeNbO_{4+\delta}$. The diffraction pattern recorded at 960 °C is shown in Figure 4. Except for a few minor diffraction lines (for example at 30°), the pattern could be indexed by a combination of the two phases CeO_2 (JCPDS 34-0394) and $CeNb_3O_9$, and no diffraction lines due to polymorphs of $CeNbO_{4+\delta}$ were observed at this temperature. Here, we have used the crystal structure of $LaNb_3O_9$ (JCPDS 72-0040) to index the diffraction lines identified to belong to $CeNb_3O_9$. Upon further heating the reflections due to these two phases disappeared, and at 1050 and 1100 °C the diffraction patterns could be indexed to tetragonal $CeNbO_{4+\delta}$.

The reoxidation observed by TGA can based on the HTXRD data and can be explained by the reaction

$$CeNbO_4 + (1/6)O_2(g) \rightleftarrows (2/3)CeO_2 + (1/3)CeNb_3O_9 \qquad (2)$$

when neglecting the minor hyper-stoichiometry of $CeNbO_4$. The weight gain is explained by the oxidation of Ce(III) to Ce(IV) due to the formation of CeO_2. The weight gain due to completion of reaction 2 would result in a weight gain corresponding to $\delta = 0.33$ in Figure 1 (marked in the figure). This is higher than experimentally observed by TGA (see Figure 1), demonstrating that the kinetics of the decomposition/oxidation reaction is slow. Finally, the reversal of reaction 2 gives the final weight loss of the sample on further heating in line with HTXRD data showing the reappearance of tetragonal $CeNbO_{4+\delta}$.

How can we understand the present observation with respect to equilibrium thermodynamics? Let us first apply the Gibbs phase rule, $Ph + F = C + 2$, where Ph, F, and C are the number of phases, degrees of freedom, and components in the system, respectively. The Ce−Nb−O system is a three component system ($C = 3$), corresponding to the three elements. At constant pressure four phases can be in equilibrium ($F = 0$, $Ph = 4$), corresponding to three condensed phases and the gas phase. The reverse of reaction 2, corresponding to reaction 3 below, which is observed by HTXRD and TGA, is therefore in equilibrium at only one temperature at 1 bar oxygen pressure.

$$(2/3)CeO_2 + (1/3)CeNb_3O_9 \rightleftarrows CeNbO_4 + (1/6)O_2(g) \qquad (3)$$

Lowering the partial pressure of oxygen would then shift the equilibrium temperature to lower temperatures. However, if the partial pressure is kept constant and the temperature is lowered, this will lead to complete decomposition/oxidation of $CeNbO_4$, resulting in only the presence of CeO_2 and $CeNb_3O_9$.

Below the tetragonal to monoclinic phase transition of $CeNbO_4$, reaction 1, the accompanied oxidation will stabilize $CeNbO_{4+\delta}$ relative to CeO_2 and $CeNb_3O_9$. This explains why reaction 2 could not be observed by TGA or HTXRD during cooling. One may therefore expect that reaction 2 is only observed in pure oxygen. However, annealing the powder from the spray pyrolysis at 650 °C in air clearly revealed the presence of CeO_2 in the powder, and $CeNbO_{4+\delta}$ could not be detected. The equilibrium temperature of reaction 3 in air is therefore probably somewhere between 650 and 800 °C. The exact temperature could not be determined due to slow kinetics.

The present observations are summarized in the diagram shown in Figure 5. The phase transition 1 is given by the solid line, while reaction 3 is given by the broken line. The results demonstrate that $CeNbO_{4+\delta}$ is metastable with respect to CeO_2 and $CeNb_3O_9$ at lower temperatures.

Conclusion

The present observations by high temperature X-ray diffraction, thermogravimetry, and dilatometry have shown that $CeNbO_{4+\delta}$ is metastable with respect to CeO_2 and $CeNb_3O_9$ at lower temperatures. The decomposition temperature is shown to decrease with decreasing partial pressure of oxygen, and decomposition of $CeNbO_{4+\delta}$ in air or lower partial pressures of oxygen is kinetically hindered.

Acknowledgment. Work was supported by the Gas Technology Centre at NTNU and The Research Council of Norway.

CM801178A