Highly Conducting Redox Stable Pyrochlore Oxides

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$A_2B_2O_7$ complex oxides with the pyrochlore structure feature a wide variety of chemical compositions and corresponding diverse electrical and physical properties. A new pyrochlore, $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, is reported and characterized in terms of structural stability and electrical properties. The material is stable to ~1450 °C in 5% H_2/N_2 and has a high electronic conductivity in a reducing atmosphere, e.g., 9 S/cm at 800 °C in 5% H_2/N_2 after high-temperature reduction. Other cation substitutions enhance the low-temperature kinetics of conductivity response to changes in oxygen partial pressure.

Introduction

$A_2B_2O_7$ pyrochlore oxides (usually A^{III}/B^{IV} and A^{II}/B^{V}) are of interest due to their diverse electrical, magnetic, dielectric, and catalytic properties[1,2] In the solid oxide fuel cell (SOFC) area, pyrochlore oxides have also received attention because of their high-temperature stability and ability to accommodate a wide range of oxygen contents and the flexible cation combinations possible on both A and B sites, enabling tailoring of the structural stability and electrical properties to meet practical application requirements. For example, $[Ln_{0.9}Ca_{0.1}]_2Ti_2O_7$ (Ln = Gd, Y, and Yb) has been found to exhibit high oxide ion conductivity at high temperatures;[3–5] and the Mo^{4+} phases $Gd_2(Ti_{1-x}Mo_x)_2O_7$ (0.1 ≤ x ≤ 0.7) show high electronic conductivity under reducing atmospheres, even though they only have a narrow stability range in p_{O_2} (oxygen partial pressure), which makes such materials potentially useful as electrolyte and anode materials in solid oxide fuel cells.[6]

Oxide anode materials are highly desirable due to several limitations of the currently widely used Ni-YSZ cermet anodes, such as carbon deposition, sensitivity to sulfur poisoning, limited redox reversibility, and microstructure disruption with oxidation/reduction, which leads to performance degradation with cycling and time. Moreover, oxide anode materials with considerable electronic and ionic conductivity are also of interest for direct oxidation of methane and hydrocarbon in SOFCs.[7,8] On the other hand, stringent demands ranging from chemical and mechanical stability under reducing environments and chemical and mechanical compatibility with other SOFC components, as well as electrocatalytic activity due to the mixed ionic and electronic conductivity, make development of oxide anode materials a challenging task.[9,10] So far, though many single-phase anode oxides have been investigated, only Sr_2MoMgO_6,[11] $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$,[12] and $Sr_4La_8Ti_{11}(Mn_{0.5}Ga_{0.5})O_{38}$[13] exhibit good performance.

Our work in this area has been concerned with the study of new candidate mixed conductors with the pyrochlore structure. This paper summarizes an investigation into the chemical stability and electrical properties of new pyrochlore compositions, such as $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, $(Yb_{1.9}Ca_{0.1})[Ti(Nb_{0.5}M_{0.5})]O_{6.95}$ (M^{3+} = Mn and Cr), and $(Yb_{1.9}Ca_{0.1})[Ti(Mo^{VI}_{0.5}Mg_{0.5})]O_{6.95}$. The strategy is to introduce elements that are air-stable in the pyrochlore structure but become reduced to confer electronic conductivity upon treatment in reducing atmospheres. This does confer high conductivity, but the slow kinetics of oxygen loss at low temperatures means that these high conductivities cannot be readily accessed below 1000 °C starting from an insulating d^0 material.

Experimental Section

$Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ and other related materials, $Ln_{0.96}Ca_{1.04}TiNbO_{6.98}$ (Ln = Y and Gd), $(Yb_{1.9}Ca_{0.1})[Ti(Nb_{0.5}M_{0.5})]O_{6.95}$ (M = Mn and Cr), and $(Yb_{1.9}Ca_{0.1})[Ti(Mo_{0.5}Mg_{0.5})]O_{6.95}$ were made via solid-state reaction. The 0.04 Ca excess in $Ln_{0.96}Ca_{1.04}TiNbO_{6.98}$ and the 0.1 Ca substitutions for Ln in other systems are expected to produce oxygen vacancies and thus confer oxide ion conductivity. High-purity (99.99%) Ln_2O_3 (Ln = Y, Yb, and Gd), $CaCO_3$, TiO_2, Cr_2O_3, MnO_2, MoO_3, and Nb_2O_5 were mixed together by ball milling for 24 h with alcohol, followed by drying, grinding, and calcination at 900 °C for 15 h and at 1100 °C for 6 h. The resulting powders were isostatically

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pressed into pellets with an Autoclave Engineers cold isostatic press under a pressure of 200 MPa. Samples were subsequently sintered in either air or 5% H_2/N_2 under empirically determined conditions at 1450 °C for 15 h to obtain the maximum density without introducing high impurity levels. The relative density of the sintered specimens, which was estimated from their geometrical dimensions and weight, was in the range of 85−95%. $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ samples were also prepared by reducing air-synthesized samples (1450 °C/15 h) in 5% H_2/N_2 at 1350 °C for 15 h to compare the electrical conductivity with that of samples synthesized directly in 5% H_2/N_2 at 1450 °C for 15 h. Sintering at 1450 °C/15 h in air resulted in a light brown color for $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, while sintering in 5% H_2/N_2 at the same temperature yields black samples. The color of $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ samples, however, did not change significantly after reduction, the samples only becoming light gray. This suggests that the introduction of niobium makes reduction to form n-type carriers easier and motivated more detailed investigation of the conductivity behavior and oxygen loss behavior under reducing conditions.

The structure of the materials was analyzed by powder X-ray diffraction (XRD) on a Panalytical X'pert Pro diffractometer (with Co Kα1 radiation). Time-of-flight neutron diffraction (ND) data were collected at room temperature on the high-resolution powder diffractometer (HRPD) at the ISIS facility, Rutherford Appleton Laboratories. The electron diffraction (ED) study was carried out on a JEOL 2000FX electron microscope equipped with an EDAX analyzer.

The standard dc four-probe method was used to measure the electrical conductivity with variation of temperature in 5% H_2/N_2 at 600−950 °C on the reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ samples that were either synthesized directly in 5% H_2/N_2 or synthesized in air then reduced in 5% H_2/N_2. Pt paste and Pt wire were used to make the four probes (which were collinear with the long dimension of the bar and spanned the two perpendicular dimensions) on rectangular bars with dimension of 1.5 × 2 × 20 mm. For the less conductive samples, including the air-synthesized $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ and $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ that were synthesized in air or in 5% H_2/N_2, two-probe ac impedance spectroscopy was used for the conductivity measurements on pellet samples (10 mm diameter 1 mm thickness) with a Solatron 1255B frequency response analyzer coupled to a SI1287A electrochemical interface, using two probes also made from Pt paste and wire. The dc conductivity was also measured isothermally as a function of oxygen partial pressure (p_{O_2}) with a range of $10^{-21}−10^{-2}$ atm, at 800 and 900 °C for the 5% H_2/N_2 and air-synthesized $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ samples. The measurements started from the low and high p_{O_2} side for these two samples, respectively. CO, CO_2, O_2, and Ar gas mixtures in the appropriate ratios were used to fix the oxygen partial pressure, which was monitored by an YSZ oxygen sensor. TGA measurements on ~50 mg powdered sample were carried out using a Seiko S-II instrument from room temperature to 950 °C (5 °C/min) under flowing O_2 with a rate of 200 mL/min.

Results and Discussion

Structure and Chemical Stability. The $A_2B_2O_6O'$ pyrochlore structure (Figure 1) is a corner-sharing network of BO_6 octahedra constructed from the 48f (O1) oxygen sites with large 110 tunnels intersecting at 8b positions (space group $Fd\bar{3}m$) occupied by O' oxygen atoms. The XRD, ED, and neutron diffraction (ND) data (Figures 2 and 3) show that both the as-made and reduced new systems $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ adopt the pyrochlore structure and
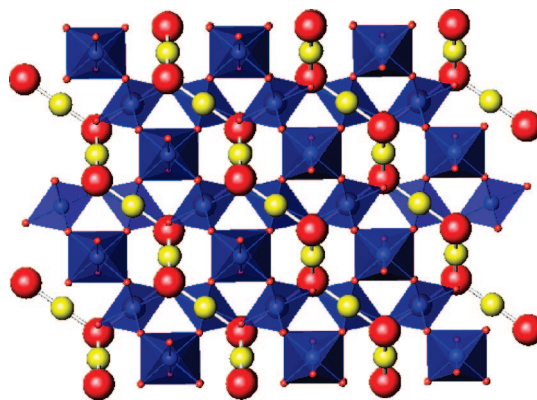

Figure 1. The BO_6 (blue octahedra) polyhedra and A_2O' sublattices (A, yellow spheres), showing two oxygen sites, 48f (O, small red spheres) and 8b (O', large red spheres).
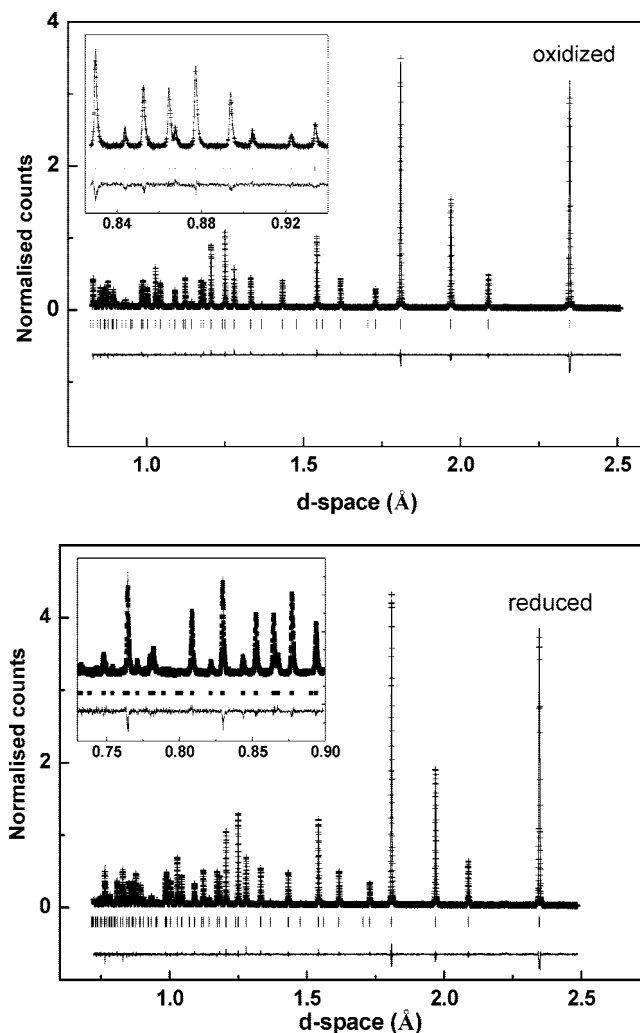

Figure 2. Rietveld refinement of neutron powder diffraction data from the back-scattering detectors for as-synthesized (in air at 1450 °C/15 h) and reduced (in 5% H_2/N_2 at 1350 °C/15 h) $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$. The upper tick marks indicate the location of individual Bragg diffraction reflections of the pyrochlore phase. The lower curve is the difference plot between the observed and calculated profiles. (Inset is a zoom of low d-space values.)

are isostructural with $Yb_2Ti_2O_7$,[4] with the 16d A site occupied by Yb/Ca and the 16c B site by Ti/Nb and two oxygen sites 48f (O1) and 8b (O2).[2] Substitutions to enhance the O vacancy content further by enhanced Ca substitution
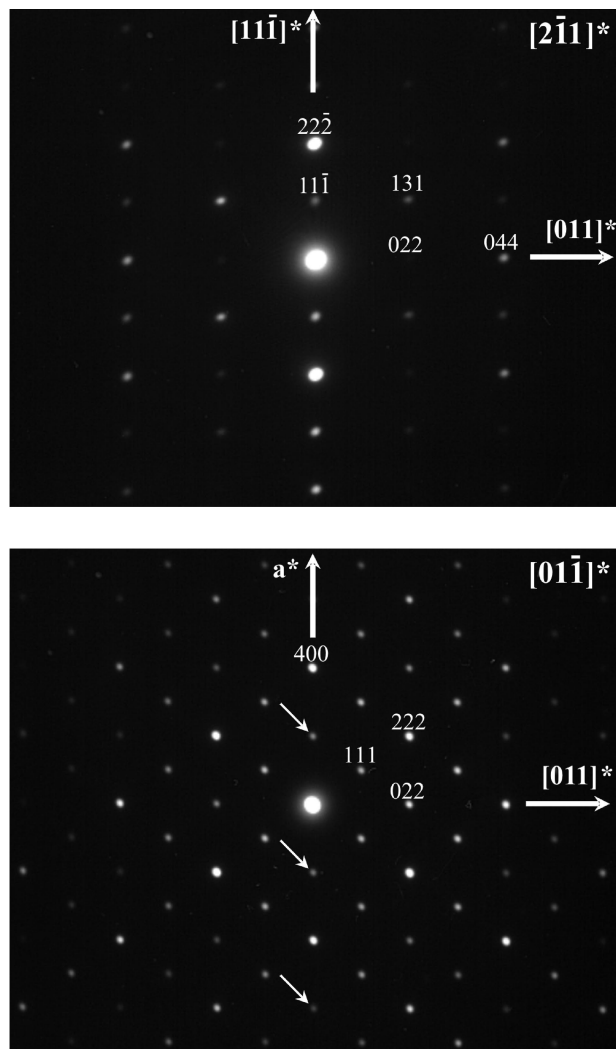
Figure 3. Electron diffraction patterns of reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ (reducing the air-synthesized sample in 5% H_2/N_2 at 1350 °C/15 h) taken from [01$\bar{1}$] and [2$\bar{1}$1] zone axes. Note that in the lower picture the reflections marked by arrows are caused by double diffraction.

Table 1. Refined Structural Parameters for Oxidized and Reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ Samples from ND Data[a]

structure parameter	oxidized	reduced
a/Å	10.22985(1)	10.22839(1)
Yb/Ca, 16c, 0.5, 0.5, 0.5		
U_{iso} (Å^2)	0.0162(2)	0.0172(1)
Ti/Nb, 16d, 0, 0, 0		
U_{iso} (Å^2)	0.0136(5)	0.0134(4)
O1, 48f, x, 0.125, 0.125	0.32381(4)	0.32403(4)
U_{iso}	0.0164(1)*/ 0.0166(1)**	0.0179(1)*/ 0.0181(1)**
occupancy	0.998(2)*/ 0.998(2)**	0.994(0)*/ 0.996(0)**
O2, 8b, 0.375, 0.375, 0.375		
U_{iso} (Å^2)	0.0164(1)*/ 0.0150(3)**	0.0179(1)*/ 0.0164(2)**
occupancy	1.001(3)*/ 0.985(3)**	0.985(3)*/ 0.971(3)**
oxygen content per formula	$O_{6.99(2)}$*/ $O_{6.97(2)}$**	$O_{6.947(3)}$*/ $O_{6.947(3)}$**
$R_p(\%)/R_{wp}(\%)/\chi^2/ R_F^2(\%)$*	5.94/6.91/1.22/3.4	5.75/7.11/1.32/5.0

[a] Occupancy of Yb/Ca/Ti/Nb is 0.48, 0.52, 0.5, and 0.5, respectively. Parameters marked with * and ** are from refinements with and without the constraints that U_{iso} values for the O1 and O2 are identical. The oxygen content of the reduced sample was constrained at the TGA result, $O_{6.92(3)}$. The reliability factors are essentially identical with and without the constraint.

at the O2 site, but when identical displacement parameters are used for the two sites, the vacancies are evenly distributed across them (Table 1). The O content for the reduced material was constrained at the value derived by TGA in reducing and oxidizing atmospheres, judged to be more reliable for the low level of oxygen vacancies present, and the corresponding values are given in Table 1. The refinement of cationic antisite disorder involving only two metal cations, i.e., M1/M2, M1 = $Yb_{0.48}Ca_{0.52}$ and M2 = $Ti_{0.5}Nb_{0.5}$, at A and B sites did not improve the fitting and led to near-zero occupancies for Yb/Ca at the B sites and for Ti/Nb at A sites. This indicates that the cationic antisite defect formation is very limited in the present system. The final refined structural parameters for the as-synthesized and reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ are listed in Table 1. There is no clear structural difference between the oxidized and reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ materials from the neutron refinements. Electron diffraction patterns (Figure 3) from a sample made by reducing the air-synthesized sample in 5% H_2/N_2 at 1350 °C for 15 h are indexed with a unit cell of 10.2 Å and reveal no evidence of obvious structural difference between the reduced and oxidized pyrochlore structures, even over the shorter length scales probed by electron diffraction.

Electrical Properties. Electrical conductivity measurements were performed on the oxidized and reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ samples that were synthesized in air and in 5% H_2/N_2, respectively, both at 1450 °C for 15 h, and then measured in the same atmosphere as used for synthesis. As shown in Figure 4, treatment in the reducing atmosphere drastically increases the conductivity: the sample as-synthesized in 5% H_2/N_2 exhibits a high conductivity, i.e., 9.0 and 11.8 S/cm at 800 and 900 °C, respectively. As a reference, Sr_2MoMgO_6 has an electrical conductivity of 4.3 S/cm in 5% H_2/N_2 at 800 °C and of 8.6 S/cm in pure H_2,[11]
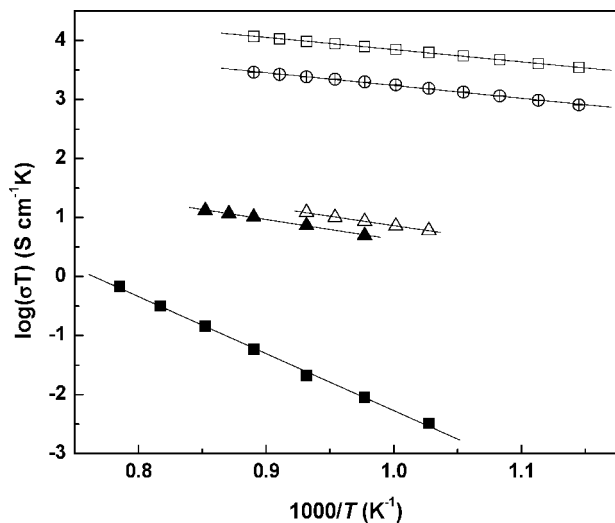
($Yb_{0.9}Ca_{1.1}TiNbO_{6.95}$ and $Yb_{0.8}Ca_{1.2}TiNbO_{6.9}$) and to reduce the Nb content ($Yb_{0.96}Ca_{1.04}Ti_{1.1}Nb_{0.9}O_{6.93}$) produce multiple phase systems. The reduced sample prepared by annealing in H_2/N_2 at 1350 °C/15 h shows no impurities by diffraction techniques, whereas XRD from the sample synthesized directly in H_2/N_2 at 1450 °C/15 h shows a trace of $CaTiO_3$ impurity, at a level too small (less than 0.1% weight) to affect the conclusions of this study. The ND data were used to refine the oxygen content and the occupancy fraction for cations (which were constrained in accordance with the nominal compositions during the refinement). The positional and isotropic atomic displacement parameters for all the sites were refined initially followed by refinement of the occupancies for O1 and O2 sites without any constraint. This led to total oxygen contents of 6.97(2) for the oxidized and 6.98(2) for the reduced sample. This agrees well with the nominal composition $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ for the air-synthesized material, assuming oxidation states +4 for Ti and +5 for Nb within error. It is difficult to identify the distribution of the small number of oxygen vacancies across the two sites. Use of different U_{iso} at the two sites produces more vacancies

Figure 4. Temperature dependence of the electrical conductivity for $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ ($\square$, $\otimes$, $\blacksquare$) and $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ ($\triangle$, $\blacktriangle$) samples that were synthesized (1450 °C/15 h) and measured in air ($\blacksquare$, $\blacktriangle$), synthesized (1450 °C/15 h) and measured in 5% H_2/N_2 ($\square$, $\triangle$), synthesized in air (1450 °C/15 h) and then reduced in 5% H_2/N_2 (1350 °C/15 h) and also measured in 5% H_2/N_2 ($\otimes$). $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ has a higher conductivity in air ($\blacktriangle$) than $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ ($\blacksquare$), but its conductivity is almost insensitive to change to a reducing atmosphere ($\triangle$), whereas that of $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ ($\square$, $\otimes$) is greatly increased.

and $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ exhibits a conductivity of 1.5 S/cm in 5% H_2/N_2 at 900 °C.[12]

The temperature dependence of the conductivity can be described by a small-polaron hopping mechanism, $\sigma T = A \exp(-E_a kT)$. The activation energy for the reduced material synthesized directly in 5% H_2/N_2 is 0.406 ± 0.002 eV over the temperature range 600–900 °C. This value is comparable with that observed for $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, 0.56 ± 0.1 eV, but higher than that of Sr_2MoMgO_6, 0.197 ± 0.021 eV; the conduction mechanism was also attributed to the small-polaron hopping in both materials.[11,12] On the other hand, the sample as-synthesized in air shows very limited conductivity, i.e., 1.21×10^{-4} S/cm at 900 °C with an activation energy of 1.917 ± 0.038 eV in the temperature interval 700–1000 °C. Figure 4 also shows the conductivity of a second $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ sample that was synthesized in air at 1450 °C/15 h and then reduced in 5% H_2/N_2 at 1350 °C/15 h. This material shows a conductivity of 2.3 S/cm at 800 °C. In comparison, a conductivity of 9 S/cm was obtained for $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ sample that was synthesized directly in 5% H_2/N_2 at 1450 °C/15 h, indicating that a higher degree of reduction leads to an increase in the electrical conductivity for the Ti/Nb pyrochlore material.

Figure 5 shows the electrical conductivity as a function of p_{O_2} for both the air and 5% H_2/N_2-synthesized sample of $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$. The conductivity increases with decreasing p_{O_2} for both samples, indicative of an n-type electronic conduction mechanism in these pyrochlores, associated with reduction of the d^0 centers. The sample as-synthesized in air shows only limited conductivity at 900 °C over the whole p_{O_2} range with a slope in the $\log \sigma$ vs p_{O_2} plot of ~0.154, which is close to a $p_{O_2}^{-1/6}$ dependence. The transition above $p_{O_2} = 10^{-5}$ atm for the 5% H_2/N_2-synthesized sample likely reflects enhanced reoxidation kinetics of quenched-in defects at higher p_{O_2} values. The
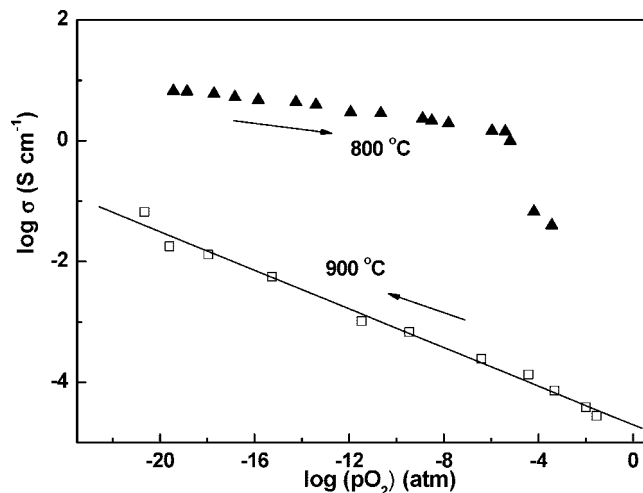

Figure 5. Electrical conductivity measured as a function of oxygen partial pressure for two $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ samples that were synthesized (1450 °C/15 h) in air ($\square$, measured at 900 °C, with $p_{O_2}^{-1/6}$ dependence indicated by the solid line) and 5% H_2/N_2 ($\blacktriangle$, measured at 800 °C), respectively.

equation for the creation of n-type charge carriers in the present pyrochlore can be described as

$$2B_B^{\times} + O_O^{\times} \overset{K}{\longleftrightarrow} 2B_B' + V_O^{\bullet\bullet} + \frac{1}{2}O_2 \qquad (1)$$
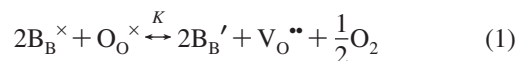
where B denotes Ti or Nb. Such that

$$K = [V_O^{\bullet\bullet}]n^2 p_{O_2}^{1/2} \qquad (2)$$

Given that the mobility μ in $\sigma = ne\mu$ is approximately constant,[14] the use of the simplified electroneutrality condition $[V_O^{\bullet\bullet}] = {}^1\!/_2[B_B']$ leads to a dependence of electronic conductivity proportional to $p_{O_2}^{-1/6}$, as observed for the air-synthesized $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ sample, in which n-type conduction is achieved mainly by lattice oxygen release through reduction. The sample synthesized in 5% H_2/N_2 exhibits a higher conductivity in the low p_{O_2}-range, but above a certain threshold p_{O_2} value, ~10^{-5} atm, the conductivity decreases sharply by approximately 2 orders of magnitude. In addition, σ is less sensitive to p_{O_2} for this sample than for the air-synthesized sample, with a slope of ~0.048 in the low p_{O_2} range below the threshold p_{O_2} value at 800 °C. The redox kinetics for these two samples also changes dramatically. At low p_{O_2} values, ~2 h is sufficient to equilibrate the 5% H_2/N_2-synthesized sample between measurements in different p_{O_2} atmospheres, whereas for the air-synthesized sample, the equilibration time is on the order of 24 h. Both these sets of observations might reflect slow oxidation–reduction kinetics, such that the measured conductivity values at these temperatures are not the equilibrium ones.

Effect of Niobium. To investigate the role of Nb in enhancing the electrical conductivity of the pyrochlore system under reducing conditions, a pure titanate of composition $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ has been synthesized and measured with the same procedure followed for $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$. The XRD pattern shows a single phase

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Table 2. Comparison between Oxidized and Reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ and $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$[a]

	$Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$		$Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$	
	oxidized	reduced	oxidized	reduced
conductivity, σ at 800 °C	1.94×10^{-5}	9.01	6.85×10^{-3}	1.20×10^{-2}
activation energy, E_a	1.917 ± 0.038 (700−1000 °C)	0.406 ± 0.002 (600−900 °C)	0.692 ± 0.017 (750−900 °C)	0.633 ± 0.017 (700 − 800 °C)
oxygen content	6.98	6.92(3)	6.98	6.98

[a] Oxidized and reduced samples were synthesized in air and 5% H_2/N_2 at 1450 °C/15 h, respectively, and measured under the same atmosphere as used in synthesis.
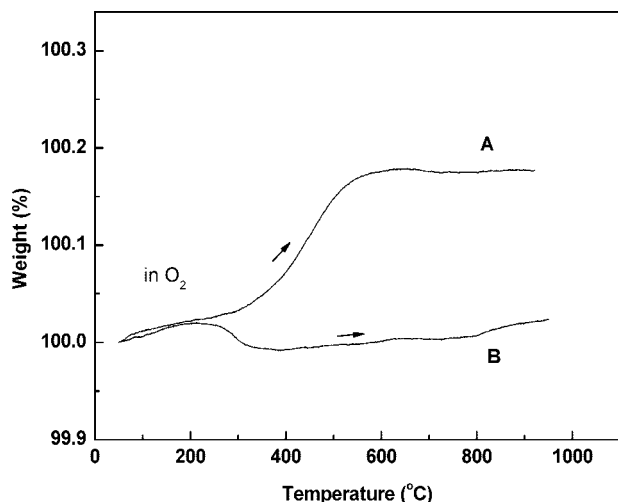

Figure 6. TGA analysis of (A) $Yb_{0.96}Ca_{1.04}TiNbO_{6.92}$ and (B) $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ (synthesized in 5% H_2/N_2 at 1450 °C/15 h). The samples were reoxidized in oxygen with a heating rate of 5 °C/min.

with the pyrochlore structure. A comparison of electrical property and TGA reoxidation results between the two systems is summarized in Table 2 and shown in Figures 4 and 6. Reduced $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ exhibits a much lower conductivity, almost 3 orders of magnitude less than that of $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, although both of them have been synthesized (at 1450 °C/15 h in 5% H_2/N_2) and measured under identical conditions and have the same starting oxygen content. Moreover, for the $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ system, reduction in 5% H_2/N_2 does not lead to a major change in the conductivity. In contrast, for the $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ samples synthesized under these two sets of conditions, the conductivity is increased by a factor of 10^5 at 800 °C. For $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$, the activation energy is calculated to be 0.633 ± 0.017 eV (700−800 °C) and 0.692 ± 0.017 eV (750−900 °C) for the reduced and oxidized samples, respectively. These values, in good agreement with previous work, could be ascribed to oxide ion migration in the pyrochlore structure,[3] indicating a negligible contribution from electronic conduction in the nominally reduced pure titanate samples. However, the reduced $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ system shows an activation energy of 0.406 ± 0.002 eV (600−900 °C), corresponding to the dominance of electronic conduction. The present study thus clearly indicates that Nb is effective for improving the electronic conductivity of pyrochlore systems under reducing conditions, with the reduction that produces the electrical conductivity in $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ taking place at Nb(V) rather than Ti(IV) to afford Nb(IV). It had been reported that Nb dopants in fluorites can increase the electronic conductivity under reducing conditions.[14] The pure titanate $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ has a higher conductivity in air than that of $Yb_{0.96}Ca_{1.04}$-

$TiNbO_{6.98}$. The electronic conductivity of a d^0 system is expected to be small and the impedance spectra for both air synthesized samples (Figure S1 of the Supporting Information) are characteristic of oxide ion conduction. This suggests that the conductivity measured in air for both the pure Ti and the Nb-substituted pyrochlore may be approximately taken as the oxide ion component.[15,16] This indicates that although Nb enhances the electronic conductivity in reducing conditions, it may produce a detrimental effect on the oxide ion transport behavior of the pyrochlore structure, because the $Nb^{5+}-O^{2-}$ bond (753 kJ/mol) is stronger than the $Ti^{4+}-O^{2-}$ (662 kJ/mol) bond, producing a trapping effect.[17] This is consistent with the slow redox equilibration kinetics of the Nb-containing sample at low temperature.

The change in oxygen content of $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ upon reduction was investigated by reoxidation of the reduced samples in a TGA experiment. Figure 6 shows the TGA analysis under oxygen for a sample that was synthesized directly in 5% H_2/N_2 at 1450 °C/15 h. A weight gain of ∼0.2% was observed on oxidation corresponding to an uptake of 0.06 oxygen atoms per formula unit. The oxidation took place between 200 and 600 °C. In comparison, $Yb_{1.96}Ca_{0.04}Ti_2O_{6.98}$ shows no observable oxygen content change between the oxidized and reduced materials, consistent with a much lower oxygen vacancy concentration than in the case of the Nb-doped system. The conductivity difference in a reducing atmosphere between the pure titanate and the Nb-containing system is correlated with the different changes in oxygen content; the pure titanate shows no observable oxygen content change between oxidized and reduced samples in the TGA study, whereas the Nb-containing system (see Figure 6) loses 0.06 oxygen atoms per formula unit. This is consistent with the enhanced ease of reduction of Nb(V) in comparison with Ti(IV) being responsible for the higher electronic conductivity under reducing conditions.

Other Doped Pyrochlore Materials. One of the major advantages of the present materials with the pyrochlore structure is that they have outstanding structural stability over a broad range of temperature (up to 1450 °C) and oxygen partial pressure ($1-10^{-21}$ atm). As a comparison, the $Gd_2(Ti_{1-x}Mo_x)_2O_7$ ($0.1 \leq x \leq 0.7$) pyrochlore system can only exist within a narrow p_{O_2} range, e.g., $10^{-12.9}-10^{-14.9}$ at 1000 °C for $Gd_2(Ti_{0.3}Mo_{0.7})_2O_7$, due to the Mo^{4+} content in these systems, which leads to decomposition into nonpyrochlore Mo^{6+} phases on heating in air.[18] $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ also has good chemical compatibility with yttria-stabilized zirconia (YSZ), that is, up to at least 1300 °C no significant chemical reaction had occurred between the two materials,

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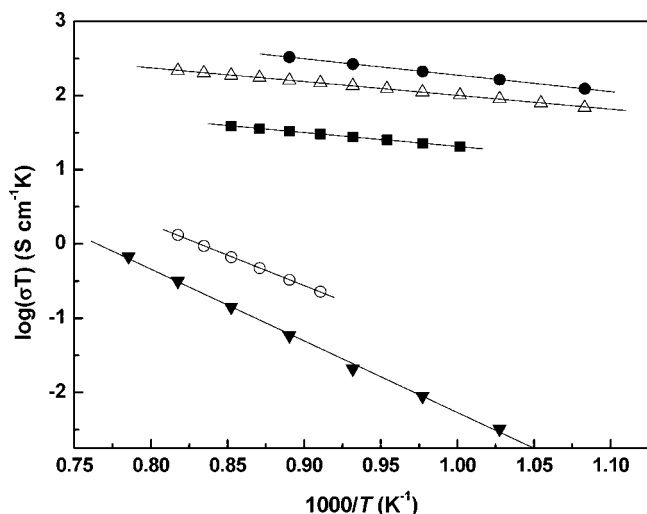(18) Sprague, J. J.; Tuller, H. L. *J. Eur. Ceram. Soc.* **1999**, *19*, 803−806.

Figure 7. Temperature dependence of the electrical conductivity for $(Yb_{1.9}Ca_{0.1})[Ti(Nb_{0.5}M_{0.5})]O_{6.95}$ (M = Mn, $\triangle$ and Cr, $\blacksquare$), $(Yb_{1.9}Ca_{0.1})$-$[Ti(Mo_{0.5}Mg_{0.5})]O_{6.95}$ ($\bigcirc$, $\bullet$), and $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ ($\blacktriangledown$) that were synthesized (1450 °C/15 h) and measured in air ($\triangle$, $\blacksquare$, $\bigcirc$, $\blacktriangledown$) and synthesized in air and then reduced in 5% H_2/N_2 (850 °C/24 h) and also measured in 5% H_2/N_2 ($\bullet$).

as shown in Figure S2 of the Supporting Information. For $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, however, the fact that a high electrical conductivity can only be obtained after reduction under extreme conditions reflects sluggish redox kinetics due to the difficulty of losing oxygen, which may in turn be associated with the very limited oxide ion conductivity in this pyrochlore system. Similar limitations have also been found in some perovskite titanates, like $La_{1-x}Sr_xTiO_3$[19] and $Sr_{1-1.5x}Y_xTiO_3$,[20] which show very low ionic conductivity and need extreme conditions for reduction to deliver appreciable electronic conductivity. Thus the n-type electrical conductivity of up to 9 S cm^{-1} at 800 °C in 5% H_2/N_2 will only be attractive for potential use as an SOFC anode if it is easily recovered from the oxidized to the reduced state after redox cycling at low temperatures.

One possible method to promote the redox activity of the present pyrochlore materials is by compositional tuning. In the pyrochlore structure of these systems, Yb can be substituted with Y or Gd, or Ti with Mn or Mg/Mo. Typical XRD patterns recorded for $Ln_{0.96}Ca_{1.04}TiNbO_{6.98}$ (La = Y and Gd), $(Yb_{1.9}Ca_{0.1})[Ti(Nb_{0.5}M_{0.5})]O_{6.95}$ (M = Mn and Cr), and $(Yb_{1.9}Ca_{0.1})[Ti(Mo_{0.5}Mg_{0.5})]O_{6.95}$ are given in Figure S3 of the Supporting Information. Single phases with the pyrochlore structure can be identified for these compositions with lattice parameters of 10.0839(3), 10.0874(4), and 10.155(3) Å for the Mn-, Cr-, and Mo-doped pyrochlores, respectively. Figure 7 summarizes the conductivity data of these materials measured in air. The B-site substitutions are more effective than the A-site substitutions for improving the electrical properties. $Ln_{0.96}Ca_{1.04}TiNbO_{6.98}$ (Ln = Y, Gd) shows similar redox kinetics and comparable conductivity after reduction to that of $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, but $(Yb_{1.9}Ca_{0.1})[Ti(Nb_{0.5}M_{0.5})]O_{6.95}$ (M = Mn and Cr) exhibit

conductivities of 0.14 and 0.03 S/cm at 850 °C in air, respectively. These values are much higher than those found for $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ (5.2 × 10^{-5} S/cm at 850 °C) under the same measurement conditions due to the introduction of the d^n cations. Introduction of an equimolar mixture of Mn or Cr with Nb(V) to substitute for Ti(IV) would suggest that both metals are present in the +3 oxidation state. This is consistent with the p_{O_2} dependence of the conductivity of both Mn- and Cr-substituted pyrochlores at 850 °C, which shows p-type conduction over the high p_{O_2} range (electrical conductivity decreases with the decreasing p_{O_2} due to oxidation introducing the +4 metal oxidation state) as shown in Figure S4 of the Supporting Information. In comparison, the introduction of Mo on the B site in $(Yb_{1.9}Ca_{0.1})[Ti(Mo_{0.5}Mg_{0.5})]O_{6.95}$ produces enhanced redox kinetics; for an air-synthesized sample, the conductivity increases from 7.0 × 10^{-4} S/cm in air to 0.3 S/cm after reduction in 5% H_2/N_2 for 24 h at 850 °C (see Figure 7) while the structure remains intact after reduction. In contrast, a conductivity value of 0.07 S/cm at 850 °C was obtained for the $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ system after reduction in 5% H_2/N_2. The oxide chemistry of Mo together with charge balance considerations strongly indicate the formation of Mo(VI) in the air-synthesized material, consistent with increased conductivity under reducing conditions.

Conclusions

A new pyrochlore system, $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$, has been synthesized and characterized in relation to potential use as a solid oxide fuel cell anode material. It has outstanding structural stability over a broad range of temperature (up to 1450 °C) and oxygen partial pressure ($1-10^{-21}$ atm), which permits the use of an air stable d^0 host to accommodate charge carriers introduced by reduction in the reduced p_{O_2} regime and thereby demonstrate mixed conductivity. Depending on the extent of reduction, $Yb_{0.96}Ca_{1.04}TiNbO_{6.98}$ possesses an electrical conductivity with values as high as 9 S/cm at 800 °C in 5% H_2/N_2. However, the sluggish redox kinetics encountered when attempting to access these reduced and highly conducting states at lower temperatures in this system are an obstacle to practical applications. Substitution of Mo onto the B-site is found to be helpful to promote the desired redox activity in the pyrochlore structure. These results motivate further attempts to optimize the redox kinetics and related electrical properties of pyrochlore-type oxides by increasing the Mo content and the search for other cations that will further enhance this behavior.

Supporting Information Available: Impedance spectra, XRD patterns showing compatibility with YSZ, XRD patterns for metal-subsituted phases, and electrical conductivity measured as a function of oxygen partial pressure for $(Yb_{1.9}Ca_{0.1})$-$[Ti(Nb_{0.5}M_{0.5})]O_{6.95}$ (M = Mn and Cr). This material is available free of charge via the Internet at http://pubs.acs.org.

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