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Oxygen Losses and Electrical Conductivity of $SrTi_{1-y}Nb_yO_{3+\delta}$ Materials

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Abstract

Porous samples were used to evaluate the changes in electrical conductivity of $SrTi_{1-y}Nb_yO_{3-\delta}$ *materials with the oxygen partial pressure; this is needed to avoid slow responses to changes in the atmosphere. The power law dependence on the oxygen partial pressure corresponds to a predominant n-type conductivity. Deviations in strongly reducing conditions were interpreted on assuming that the charge imbalance caused by niobium additions may change with the working conditions. This defect chemistry model was confirmed by varying the oxygen partial pressure in the atmosphere. A coulometric titration technique was used to evaluate the changes in oxygen stoichiometry. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Recent studies show that strontium titanate-based ceramic materials may be used for high temperature applications such as resistive sensors,[1–3] relying on a suitable dependence of conductivity on the oxygen partial pressure. The dependence expected for a dominant n-type conductivity should be nearly described by a power law $\sigma = \sigma_1 Po_2^{-1/n}$, ($\sigma$ being the electrical conductivity and Po_2 the oxygen partial pressure), especially for reducing conditions. This dependence may be observed in wider ranges of working conditions by adding a suitable donor, such as La for Sr substitutions,[4,5] or Nb for Ti substitution.[4,6] The defect chemistry model proposed by some authors[7] includes a plateau where $n \approx [Nb^{\bullet}_{Ti}]$.

The results obtained for some La-doped strontium titanate samples showed an odd dependence of conductivity on the oxygen partial pressure,[4] possibly because the response time of this type of materials is very long. Other authors thus used very high working temperatures to obtain reliable measurements.[7] The results reported in this work were obtained with porous samples as reported elsewhere.[8]

Strontium titanate can dissolve high fractions of donor additives such as lanthanum oxide,[9,10] or niobium oxide.[11] These materials undergo weight losses in reducing conditions which were interpreted on assuming a change in charge compensation, as described by[9,10]

$$SrO_{ex} + V''_{Sr} \Longleftrightarrow 1/2O_2 + 2e' + Sr^{x}_{Sr} \qquad (1)$$

where SrO_{ex} denotes a generic source/sink for the excess of SrO (e.g. a Ruddelsden–Popper type of phase).

Irvine and co authors[11] found that reduction causes significant increase in lattice parameter of $Sr_{1-y/2}Ti_{1-y}Nb_yO_{3-\delta}$ materials (at 930 °C), which was attributed to a reduction of Ti^{4+} to Ti^{3+} or Nb^{5+} to Nb^{4+}; this suggests a relatively high concentration of localised electronic carriers in reducing conditions. The excess of SrO should be negligible in these A-site deficient compositions. However, materials with unit A:B site ratio ($SrTi_{1-y}Nb_yO_{3-\delta}$) may yield segregation of SrO,[8] thus confirming that strontium vacancies should be present, at least in air. The maximum concentration of strontium vacancies expected in oxidising conditions is $[V''_{Sr}]_{max} = [Nb^{\bullet}_{Ti}]/2$.

Equation (1) also shows that the response to changes in the atmosphere may be relatively fast if the sources/sinks of SrO are located near the surface. Otherwise, the response time may be dependent on slow transport of oxygen and/or strontium vacancies to ensure migration of oxygen or strontium oxide. One may then attempt to describe the effects of composition and working conditions on the concentration of oxygen vacancies by introducing the additional reaction

$$O_o^{x} \Longleftrightarrow 1/2O_2 + 2e' + V_o^{\bullet\bullet} \qquad (2)$$

Nb-additions are expected to enhance the concentrations of strontium vacancies and electrons,

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*To whom correspondence should be addressed. Fax: +34-351-34-25300; e-mail: jfrade@cv.ua.pt and combination with the mass action laws of reactions (1) and (2) suggests a suppression of the concentration of oxygen vacancies, (in identical working conditions). Very reducing conditions may counteract this effect.

2 Experimental Procedure

Powders of $SrTi_{1-y}Nb_yO_{3+\delta}$ ($y = 0.05$ and 0.1), were prepared by solid state reaction from $SrCO_3$, TiO_2, and Nb_2O_5 in the required proportions. These reactants were mixed together with ethanol, and calcined at 1100 °C, for 15 h. Calcined powders were milled to destroy the agglomerates, and used to prepare pellets which were fired at temperatures in the range 1200–1600 °C, depending on the required density. SEM and EDS were used as a preliminary assessment of average grain size and porosity, and to inspect the segregation of second phases. X-ray diffraction was used to confirm the cubic perovskite structure of these materials, and to evaluate the theoretical density. An Archimedes method was used to evaluate the apparent density.

A four wires dc method was used to measure the electrical conductivity at temperatures in the range 800–1000 °C, and as a function of the oxygen partial pressure, in a furnace equipped with a potentiometric oxygen sensor, and an electrochemical oxygen pump. The pump was used to attain very reducing conditions, and measurements were performed on reducing and also on reoxidizing the samples. The behaviour of the samples was assessed from the extreme ranges of very reducing and oxidising conditions only (Figs 1 and 2). In fact, the oxygen sensors fail in intermediate ranges of oxygen partial pressures, when the atmosphere is easily disturbed by minor leaks, and looses its buffer effect;[12] this is responsible for the apparent hysteresis shown on cycling from oxidising to reducing and then back to oxidising conditions (shown in Figs 4 and 5).

Coulometric titration measurements were performed using a method derived from a technique proposed elsewhere.[13] The cell which was used in this work comprises a device for pumping out oxygen, and an oxygen sensor to measure the oxygen partial pressure inside the cell. Using powders rather than bulk samples lowers the time required to attain equilibrium between the sample and the atmosphere inside the cell.

The oxygen stoichiometry was evaluated on integrating current changes after step changes in applied voltage; this yields

$$\Delta\delta = \{M/(2Fm)\} \int_{0'} (I - I_L)\,dt' \qquad (3)$$

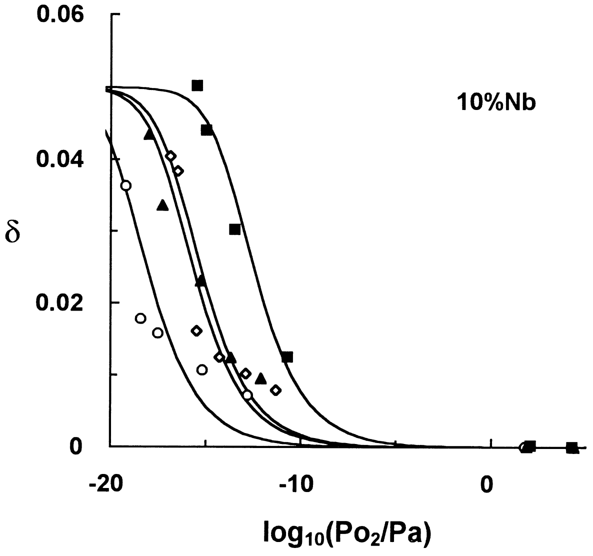

Fig. 1. Changes in oxygen stoichiometry of $SrTi_{0.9}Nb_{0.1}O_{3+\delta}$ versus oxygen partial pressure at 850°C (circles), 900°C (triangles), 950°C (losangles), and 1000°C (squares).

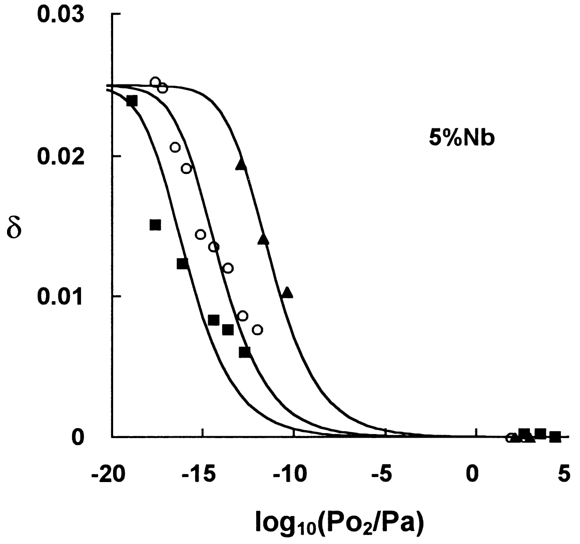

Fig. 2. Changes in oxygen stoichiometry of $SrTi_{0.95}Nb_{0.05}O_{3+\delta}$ versus oxygen partial pressure at 900°C (squares), 950°C (circles), and 1050°C (triangles).

where M denotes the molecular weight of $SrTi_{1-y}Nb_yO_{3+y/2}$, m is the mass of the sample, F is the Faraday constant, and I_L is the residual current due to minor leaks. The oxygen stoichiometry in air is expected to converge to the upper value $\delta_{max} = y/2$ in oxidising conditions; this corresponds to segregation of SrO in Ruddelsden–Popper phases.

3 Weight Changes versus Defect Chemistry

A model behaviour was proposed elsewhere[8] to describe the defect chemistry of the actual $SrT_{1-y}Nb_yO_{3+\delta}$ materials. This model was based on a simplified neutrality condition

$$n + 2[V''_{Sr}] = [Nb^{\bullet}_{Ti}] \qquad (4)$$

combined with the equilibrium constant of eqn (1)

$$K_1 = \mathrm{Po}_2^{1/2} n^2 / \{[V''_{\mathrm{sr}}] a_{\mathrm{SrO}}\} \qquad (5)$$

where a_{SrO} denotes the activity of SrO, and the Kroger–Vink notation is used for the remaining variables. On assuming nearly unit activity ($a_{\mathrm{SrO}} \approx 1$) one easily obtains

$$[V''_{sr}]/[\mathrm{Nb}^{\bullet}_{\mathrm{Ti}}] = 0.5 - 0.5(P_x/\mathrm{Po}_2)^{1/4} \left\{\left[1 + 0.25(P_x/\mathrm{Po}_2)^{1/2}\right]^{1/2} - 0.5(P_x/\mathrm{Po}_2)^{1/4}\right\} \qquad (6)$$

with

$$P_x = \{0.5\ \mathrm{K}_1 a_{\mathrm{SrO}}/[\mathrm{Nb}^{\bullet}_{\mathrm{Ti}}]\}^2 \qquad (7)$$

This parameter represents the oxygen partial pressure required to change the main charge compensation species. The limiting trends are $[V''_{\mathrm{sr}}] \approx [\mathrm{Nb}^{\bullet}_{\mathrm{Ti}}]/2$ in oxidising conditions, and $n \approx [\mathrm{Nb}^{\bullet}_{\mathrm{Ti}}]$ for sufficiently reducing conditions.

The concentration of strontium vacancies is also a measure of the changes in oxygen stoichiometry of $\mathrm{SrTi}_{1-y}\mathrm{Nb}_y\mathrm{O}_{3+\delta}$ materials [(see eqn (1)], and eqn (6) thus corresponds to:

$$\delta = y/2 - (y/2)(P_x/\mathrm{Po}_2)^{1/2}]^{1/2} - 0.5(P_x/\mathrm{Po}_2)^{1/4}\} \qquad (8)$$

y being the fraction of Nb for Ti substitution. The stoichiometry attained on reaching the oxygen partial pressure $\mathrm{Po}_2 = P_x$ is $\delta = 0.191y$.

Equation (8) was used to fit the results obtained by coulometric titration (Figs 1 and 2). The agreement is relatively good, but the actual working conditions were probably insufficient to attain the limiting plateau (expected for very reducing conditions). Extremely reducing conditions were avoided to prevent the onset of electronic conductivity of the YSZ components of the cell, and the corresponding electrochemical permeability.

The values of fitting parameter P_x extracted from the dependence of oxygen stoichiometry on the oxygen partial pressure are also shown in Fig. 3. The corresponding values of activation are 908 kJ mol^{-1} for 5%Nb, and 929 kJ mol^{-1} for 10%Nb.

4 Electrical Properties

When exposed to changes from very reducing to oxidising conditions the response times of porous samples are at least three orders of magnitude smaller than the response times of the corresponding dense pellets, as shown elsewhere.[8] The size, and time scales yield similar ranges of dimensionless time tD/L^2 for dense and porous samples, L being the thickness of a dense sample or a typical grain size for porous samples; this suggests oxygen uptake from the atmosphere, and diffusion controlled behaviour. Porous samples were thus suitable to attain stable readings in short times, and were used to evaluate the dependence of conductivity on the oxygen partial pressure, and temperature, as shown in Figs 4 and 5.

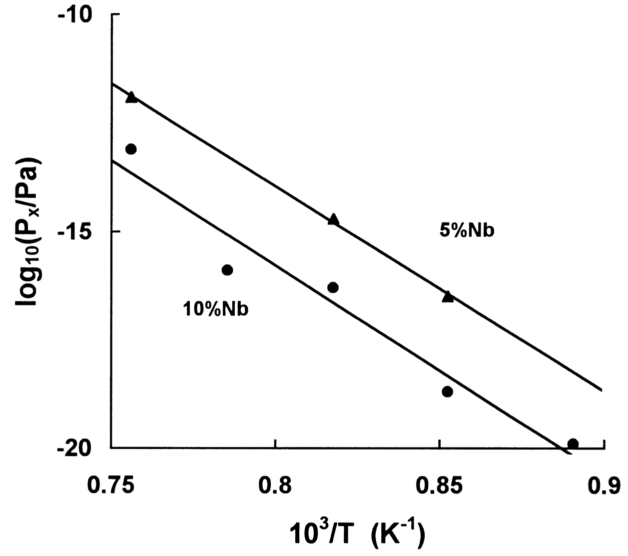

Fig. 3. Temperature dependence of P_x obtained by fitting the changes in oxygen stoichiometry with eqn (6) (closed symbols).

The dependence of the concentration of the main charge carrier (n) on the oxygen partial pressure is easily predicted on combining eqns (4) and (6). A similar dependence is expected for the n-type conductivity, and on adding a residual p-type contribution one obtains:[8]

$$\sigma = \sigma_{n1}(\mathrm{Po}_2)^{-1/4}\left\{\left[1 + 0.25(P_x/\mathrm{Po}_2)^{1/2}\right]^{1/2} - 0.5(P_x/\mathrm{Po}_2)^{1/4}\right\} + \sigma_{p1}\mathrm{Po}_2^{1/4} \qquad (9)$$

where σ_{n1} and σ_{p1} are the n-type and p-type conductivity contributions at unit oxygen partial pressure. Note that some results suggest the onset of a p-type contribution ($\sigma_p \mathrm{Po}_2^{1/4}$) in oxidising conditions.

Equation (9) was drawn in Figs 4 and 5 with values of Po_2 extracted from the weight losses (Fig. 3). The remaining fitting parameters (σ_{n1} and σ_{p1}) were adjusted to minimise the differences between eqn (9) and experimental data in reducing and oxidising conditions. The agreement is relatively good for 5%Nb (Fig. 4) except in the intermediate range, where the oxygen sensor fails.[12] This experimental limitation may affect the results obtained for different materials, especially when the conductivity is nearly described by a generic

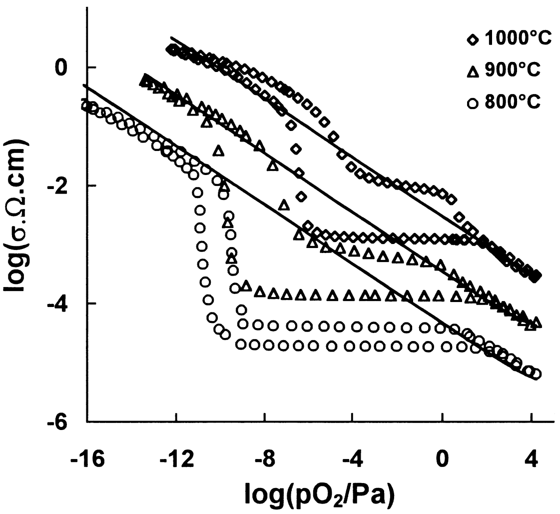

Fig. 4. Conductivity of $SrTi_{0.95}Nb_{0.05}O_{3+\delta}$ versus oxygen partial pressure at 800, 900 and 1000°C. The solid lines represent eqn (9).

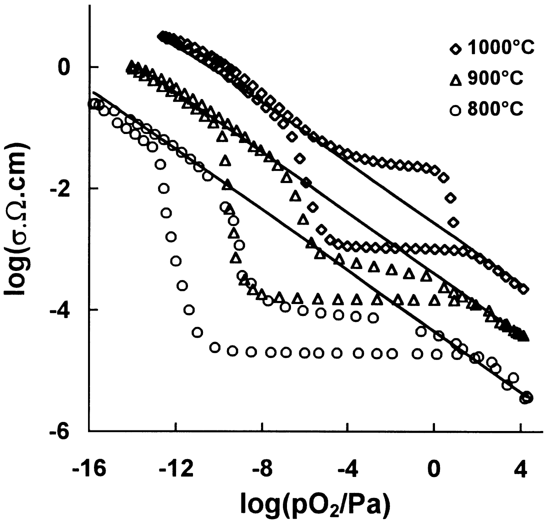

Fig. 5. Conductivity of $SrTi_{0.9}Nb_{0.1}O_{3+\delta}$ versus oxygen partial pressure at 800, 900, and 1000°C. The solid lines represent eqn (9).

power $\sigma = \sigma_1(Po_2)^{\pm 1/4}$ in the intermediate range of oxygen partial pressure.

The results for 5% (Fig. 4) show that the deviations from a limiting $-1/4$ slope occur for values of Po_2 which are somewhat higher than the order of magnitude of the values of P_x extracted from coulometric titration results. These deviations may suggest an alternative regime. For example, on assuming that the defect chemistry is controlled by eqn (2) one obtains a neutrality condition $n \approx 2[V_o^{\bullet\bullet}]$, and this should yield a slope $-1/6$ on plotting $\log(\sigma)$ versus $\log(Po_2)$.

5 Conclusions

A relatively simple coulometric titration was successfully used to evaluate the oxygen stoichiometry of $SrTi_{1-y}Nb_yO_{3+\delta}$ versus the working conditions (temperature, and oxygen partial pressure). These results are consistent with the dependence of conductivity $SrTi_{0.9}Nb_{0.1}O_{3+\delta}$ on Po_2, and both types of results may be interpreted on assuming a change in charge compensation from $[V''_{sr}] \approx [Nb^{\bullet}_{Ti}]/2$ (in oxidising conditions) to $n \approx [Nb_{Ti^{\bullet}}]$ (in reducing conditions). The transition between these regimes varies with temperature, and the corresponding values of activation energy is about 908 kJ mol^{-1} for 5%Nb, and 929 kJ mol^{-1} for 10%Nb. However, the transition tends to be shifted towards more reducing conditions with increasing Nb content.

Acknowledgements

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