Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solid State Ionics 177 (2006) 1129 – 1135
SOLID STATE IONICS
www.elsevier.com/locate/ssi

High-temperature proton conductivity in acceptor-doped $LaNbO_4$

Reidar Haugsrud *, Truls Norby

Department of Chemistry, University of Oslo, Centre for Materials Science and Nanotechnology, P.O. Box 1126 Blindern, N-0318 Oslo, Norway

Received 26 January 2006; received in revised form 19 April 2006; accepted 9 May 2006

Abstract

The conductivity of acceptor-doped $LaNbO_4$ has been investigated in the temperature range 300 to 1200 °C as a function of the oxygen pressure and water vapor pressure by means of impedance spectroscopy and EMF measurements. The conductivity is predominantly ionic below 800 °C in air and for higher temperatures under reducing conditions. Protons are the major ionic charge carrier in the presence of water vapor. A maximum in proton conductivity of ~0.001 S/cm was obtained at 950 °C in atmospheres containing ca 2% H_2O. At high temperatures (>1000 °C) under oxidizing conditions, electron hole conduction prevails. The conductivity has been modeled assuming that oxygen vacancies and protons compensate the acceptor doping. Transport coefficients describing mobility of defects and thermodynamic constants for the incorporation of protons have been derived.

Keywords: Acceptor-doped $LaNbO_4$; Proton conductivity; Defect structure; Thermodynamic relations; Transport coefficients

---

1. Introduction

Materials with transport of protons are interesting for a number of low and high temperature industrial applications. Since hydrogen is one of the major chemical energy carriers, proton conductors can be utilized in processes related to conversion between chemical energy and electricity. This may for example be as a purely ionic conductor serving as an electrolyte in a high-temperature solid oxide fuel cell (SOFC), or as a mixed high-temperature protonic–electronic conductor in a membrane for hydrogen separation.

High-temperature proton conductors have, in general, been found to be oxides with oxygen deficiency in the form of oxygen vacancies, where protons dissolve as hydroxide defects ($OH_O^{\bullet}$) in the oxide at the expense of the vacancies. Acceptor-doped perovskites are examples of oxides containing both oxygen vacancies and protons. Some of the Ba and Sr containing perovskites exhibit state-of-the-art proton conductivity of about 0.01 S/cm (e.g. $BaCe_{0.9}Y_{0.1}O_{3-\delta}$) [1–4]. One major limitation of these perovskites with respect to industrial utilization is that they decompose in CO_2-containing atmospheres [5]. Since these materials are essentially pure ionic conductors, their performance as hydrogen-permeable gas separation membranes will be limited by the relatively low electronic conductivity [3].

Oxides that are more stable in CO_2-containing atmospheres show more than one order of magnitude lower proton conductivity than the above-mentioned perovskites. Norby et al. [6–8] demonstrated that acceptor-doped rare-earth sesquioxides conduct protons, where the maximum conductivity, 7.5×10^{-4} S/cm, was observed for Ca-doped Gd_2O_3 (900 °C). Rare-earth phosphates form another class of CO_2-tolerant materials with appreciable proton conductivity [9–11]. Acceptor-doped LaP_3O_9 exhibits the highest proton conductivity of these phosphates, in the order of 3×10^{-4} S/cm (700 °C). However, the stability of this material is limited with respect to temperature. Rare-earth oxides and phosphates investigated so far are essentially pure ionic conductors and represent, as such, not prime candidate materials for stand-alone hydrogen separation membranes.

This paper presents results of an investigation of proton conductivity in acceptor-doped $LaNbO_4$. The conductivity characteristics have been investigated as a function of the oxygen pressure and water vapor pressure in the temperature range 300 to 1200 °C. The measurements have been performed by means of AC impedance spectroscopy and the partial

---

* Corresponding author. Tel.: +47 22 84 06 59; fax: +47 22 84 06 51.
E-mail address: reidarha@kjemi.uio.no (R. Haugsrud).

0167-2738/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2006.05.011

conductivities have, furthermore, been determined from the EMF of hydrogen and oxygen concentration cells. The present contribution is one in a series describing the electrical properties of acceptor-doped rare-earth orthoniobates and orthotantalates with emphasis on proton conduction [12,13].

2. Structure and defect structure of acceptor-doped $LaNbO_4$

$LaNbO_4$ exists as two different polymorphs, depending on the temperature [14,15]. The low-temperature phase is monoclinic and corresponds to the Fergusonite-type structure, whereas the high-temperature phase is tetragonal corresponding to the Scheelite structure. The transition between these two phases has been reported in the temperature range 500 to 530 °C [16–18].

Teterin et al. [19] measured the conductivity of a number of different undoped rare-earth niobates and found that the total conductivity, depending on temperature and oxygen pressure, showed both ionic and electronic characteristics.

For a nominally undoped material, an ionic regime encountered as an oxygen pressure independent regime in the conductivity may occur as a consequence of intrinsic ionic disorder (typically of Schottky-type). However, one often finds that the level of aliovalent impurities surpasses the intrinsic defects, resulting in an ionic regime. In our case we want to deliberately increase the concentration of effectively positive native point-defects – presumably oxygen vacancies – by substituting Ca^{2+} for La^{3+}:

$$2CaO + Nb_2O_5 = 2Ca'_{La} + 2Nb^x_{Nb} + V^{\cdot\cdot}_O + 7O^x_O \qquad (1)$$

Here, the concentration of oxygen vacancies becomes independent of temperature and the ambient oxygen pressure, provided that the doping concentration is below the solubility limit and, moreover, exceeds the concentration of the intrinsic electronic defects.

$LaNbO_4$ may have a tendency to dissolve protons by interacting e.g. with ambient water vapor:

$$H_2O(g) + V^{\cdot\cdot}_O + O^x_O = 2OH^{\cdot}_O \qquad (2)$$

Now by assuming that the acceptor is compensated by oxygen vacancies and protons, the electroneutrality condition requires that:

$$[Ca'_{La}] = 2\left[V^{\cdot\cdot}_O\right] + \left[OH^{\cdot}_O\right]. \qquad (3)$$

The brackets denote concentrations of the respective defects.

Eqs. (1)-(3) represent the defect structure often encountered for acceptor-doped oxides dissolving protons. Kreuer [20], Larring [21] and Haugsrud and Norby [12] have solved such defect systems with the purpose of modeling thermodynamic and kinetic parameters on the basis of experimental results, e.g. thermogravimetry of dissolution of water and conductivity measurements. A similar approach has been followed in modeling of the experimental data within this contribution.

3. Experimental

Acceptor-doped $LaNbO_4$ has been synthesized by mixing nominal amounts of oxide powders, La_2O_3, Nb_2O_5 and either $SrCO_3$ or $CaCO_3$, in an agate planetary ball mill for 20 min in isopropanol. After evaporating the isopropanol, the powder mixture was uniaxially cold pressed into pellets and calcined in air at 1000 °C for 15 h. The pellets were crushed and, similarly re-milled and calcined over again three times. Powder X-ray diffraction revealed that single-phase $LaNbO_4$ corresponding to the Fergusonite structure was formed. In some cases (Sr doping), traces of the high-temperature tetragonal Scheelite structure were present. The powder was uniaxially cold-pressed in a 25 mm die at 5.5 Tonn and sintered at 1500 °C for 5 h. The final disc specimens had relative densities between 93% and 97%, with grain sizes of 5 to 10 μm.

Circular Pt electrodes of diameter ~1 cm were attached to each side of the specimen by first painting one layer with Pt ink (Metallor, Pt A3788A), then adding a Pt net followed by painting of a few more layers with ink. The specimens with electrodes were annealed at 1000 °C for 1 h to burn off residual organics from the Pt ink.

The electrical characterization of $LaNbO_4$ was performed in a Probostat™ measurement cell [22]. The specimen was on top of an inner alumina support tube. For experiments where the purpose was to measure partial conductivities by EMF concentration cell technique, a 1 mm thick gold gasket was placed between the specimen and the support tube. By means of an outer closed alumina tube, the assembly forms two gas volumes separated by the specimen. Electrode leads from the cell base were attached to the circular electrodes on the specimen – from underneath inside the inner compartment, and on top of the specimen, from the outer gas compartment. Relatively strong spring loads held the whole assembly together, to maintain contact between the Pt leads and the electrodes at the surface of the specimen and to facilitate the gold sealing. The inner and the outer compartment were connected to a gas mixer so as to establish well-defined gradients in oxygen, hydrogen and water vapor across the specimen. After heating to ~1060 °C to soften the gold gasket, essentially no leakage was detected between the two gas volumes (He and Ar) as probed with a quadrupole mass spectrometer on the gas outlets.

The total conductivity was measured as a function of the oxygen and water vapor pressure in the temperature range 300 to 1200 °C at a constant frequency of 10 kHz with an oscillation voltage of 0.5–1 V RMS using a Solartron 1260 FRA. In addition, impedance spectroscopy was performed in the frequency range 0.5 to 10^6 Hz under reducing conditions to determine the different contributions of bulk, grain boundaries and electrodes to the overall measured resistance. The spectra were deconvoluted using the Equivalent Circuit for Windows program [23].

The open-circuit voltage (OCV) resulting from differences in the chemical potentials across the specimen induced by gas gradients was measured with a Solartron 7150plus multimeter. In this respect, one should note that voltages measured above