Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Solid State Chemistry 179 (2006) 1469–1477

JOURNAL OF
SOLID STATE
CHEMISTRY

www.elsevier.com/locate/jssc

The defect chemistry of Ce(Pr, Zr)$O_{2-\delta}$

D.P. Fagg*, J.R. Frade, V.V. Kharton, I.P. Marozau

Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Received 18 October 2005; received in revised form 10 January 2006; accepted 28 January 2006
Available online 28 February 2006

Abstract

The influence of composition upon resultant mixed conductivity is analysed for the fluorite-type compositions $Zr_{0.1}Ce_{0.7}Pr_{0.2}O_{2-\delta}$, and $Ce_{0.8}Pr_{0.2}O_{2-\delta}$. Measurements of oxygen concentration cell e.m.f. combined with impedance spectroscopy at elevated temperatures reveal the materials to be predominantly ionic conductors in oxidising conditions and to show a decrease in both ionic and electronic conductivities with decreasing pO_2. Ion transference numbers measured under these conditions show a positive temperature dependence, with typical values $t_0 = 0.8$ and 0.9, respectively, for the two compositions at 950 °C. The combination of this information with results of coulombic titration, facilitates analysis of the pO_2 dependence of total conductivity measured by a steady-state electrochemical technique between air and reducing conditions. In more oxidising conditions, depletion of total conductivity with decreasing pO_2 results predominantly from a decreasing ionic conductivity. This is one of first examples in the literature where a fluorite-type material is shown indisputably to exhibit such behaviour. These materials show significant levels of mixed conductivity in both reducing and oxidising conditions. In more reducing conditions, an increase in total conductivity is related to increased n-type conductivity upon the reduction of cerium.

Keywords: Praseodymium-cerium oxide; Transference number; Mixed conduction; Defect chemistry; Ionic conductivity

1. Introduction

Interest has been shown for the use of ceria-based oxides as possible oxygen separation membranes, components for solid oxide fuel cells (SOFC), amperometric oxygen sensors and oxygen storage materials. Of these studies, the solid solution system $Ce_{1-x}Pr_xO_{2-\delta}$ has generated attention due to its ability to accommodate extensive deviations from stoichiometry with high rates of oxygen exchange and diffusion, whilst offering good stability in repeated redox cycles, all features of great importance for use as gas sensors, catalyst supports and/or oxygen storage materials in automotive catalysis [1–7]. These materials may also be promising for oxygen separation membranes, with oxygen permeabilities rivalling that of mixed conductors based on the best conductive bismuth oxide solid electrolytes [8]. To maximise oxygen flux through an oxygen separation membrane, mixed conductors that offer equally high electronic and ionic conductivities are required. Shuk and Greenblatt [8] demonstrated that at Pr concentrations greater than 25 at% Pr the electronic conductivity of the system $Ce_{1-x}Pr_xO_{2-\delta}$ in air starts to exceed that of the ionic conductivity, yielding theoretical values of oxygen permeability for this material, $J(O_2) = 1.9 \times 10^{-10}$ mol/scm at 700 °C.

Unfortunately the binary system, $Ce_{1-x}Pr_xO_{2-\delta}$, is blighted by a high and non-linear thermal expansion, for example, the average thermal expansion coefficient (TEC) observed by dilatometry for the material $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ is reported to vary between 10 and $30 \times 10^{-6}\,K^{-1}$ across different temperature ranges between 0 and 1000 °C [9,10]. Such a fluctuation of TEC clearly limits possible practical uses. However, recent work by our group [11] has shown that the extremely high TEC observed at intermediate temperatures in these materials has its root in the loss of oxygen upon heating and can be substantially decreased by the substitution 10 at% Zr for cerium. For example, upon substitution of 10 at% Zr for cerium to form the composition $Zr_{0.1}Ce_{0.7}\,Pr_{0.2}O_{2-\delta}$, average TECs varying

---

*Corresponding author. Fax: +351 234 425300.
E-mail address: duncan@cv.ua.pt (D.P. Fagg).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.01.052

between 13 and $18\times10^{-6}\,K^{-1}$ across the temperature range 30–1000 °C can be offered. Zirconium substitution was shown to increase average grain size, to decrease lattice parameter and to also have the negative effect of decreasing total conductivity in air. To understand this phenomenon further, we assess the influence of zirconium substitution on resultant average Pr oxidation state and study its dependence on oxygen partial pressure by use of the coulombic titration technique. Uniting these results with ion transference numbers obtained by oxygen concentration cell e.m.f. under various oxygen chemical potential gradients, will allow analysis of the pO_2 dependence of total conductivity measured for compositions $Zr_{0.1}Ce_{0.7}Pr_{0.2}O_{2-\delta}$, and $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ by a steady-state electrochemical technique.

2. Experimental

2.1. Sample preparation

Stoichiometric amounts of high-purity Pr_6O_{11}, $ZrO(NO_3)_2\cdot H_2O$, and $Ce(NO_3)_3\cdot 6H_2O$ were dissolved in a hot aqueous solution of nitric acid. After drying, the nitrate mixture was decomposed at 700 °C. The resultant powder was ball-milled in a nylon mill with zirconia balls. The milled powder was dry pressed into pellets (diameter of 20 mm, pressure of 30 MPa) followed by isostatic pressing at 200 MPa. These pellets were then sintered at 1600 °C for 10 h followed by cooling at 2 °C/min. The density of materials synthesised from their component metal nitrates was greater than 90% that of the theoretical density in every case. All samples were gas tight. Overall phase composition was determined by X-ray diffraction (XRD) using a Rigaku Geigerflex diffractometer (Cu$K\alpha$ radiation), (5–80°, step 0.02, 0.4 s/step); unit cell parameters were determined using Materials Data Inc. Jade6 software, pseudo voight profile fit and an external silicon standard for zero point correction, Table 1. All samples were single-phase cubic defect fluorite.

2.2. Electrical characterisation

Total conductivity was performed on dense bars, approximately 2 mm × 4 mm × 12 mm using the 4-point d.c. method as described elsewhere [12]. The measurements were carried out in a controlled atmosphere device consisting of a yttria-stabilised zirconia (YSZ) cell with an electrochemical oxygen pump and a sensor [12]. At the start of the experiment, the cell was filled with a gas mixture containing 50% of O_2 and 50% of CO_2 and then sealed. The conductivity was measured using a voltmeter Solartron 7081 in the temperature range 750–950 °C at oxygen partial pressures from 10^{-19} to 0.5 atm. Precise variation or maintenance of the partial oxygen pressure in the chamber was provided by the operation of the oxygen pump and sensor, controlled by a computer using specially developed software. The measurements were carried out in the mode of decreasing oxygen partial pressure in isothermal runs. When maintaining a constant oxygen pressure in the well-known instability range [13] corresponding to the electrochemical sensor e.m.f. from approximately 200 to 650–700 mV, the operation regime of the oxygen pump utilised provided the sensor e.m.f. constant with an accuracy of ±2 mV. Experimental data points were collected upon achievement of equilibrium between the sample and ambient atmosphere; the criterion of the equilibrium achieved was a conductivity relaxation rate less than 0.1% per minute, under a fixed oxygen pressure inside the chamber. The conductivity relaxation time after a change in the oxygen pressure over a sample varied up to several hours, depending on temperature, oxygen partial pressure and sample composition. As a rule, the conductivity relaxation time in the instability range was no less than 1 h; the total time necessary for one isothermal measurement cycle was 20–70 h. The above-described criteria are believed to ensure that the obtained conductivity data correspond to equilibrium oxygen content in the samples. Upon achievement of the desirable low oxygen-pressure limit, the measurements were halted and then the oxygen pressure was increased to the starting upper limit, where the measurements were repeated in order to confirm reversibility of the experiment; thereupon temperature was changed thus enabling next measuring cycle. Simultaneous measurements of thermoelectric power were obtained as described elsewhere [12].

Trace electron–hole conductivity was separated from total electrical conductivity using the modified e.m.f. method first proposed by Gorelov [14]. This modification of the classical e.m.f. technique, based on determination of the open-circuit voltage of oxygen concentration cells, increases measurement sensitivity and eliminates possible errors in the determination of ion transference numbers

Table 1
Lattice parameter and relative density of $Ce_{1-x}Pr_xO_{2-\delta}$ and $Zr_{0.1}Ce_{0.9-x}Pr_xO_{2-\delta}$ ceramics as prepared in air, together with activation energies for the partial ionic conductivities of $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ and $Zr_{0.1}Ce_{0.6}Pr_{0.2}O_{2-\delta}$ ceramics in the oxygen potential gradients 101/21 kPa and 21 kPa/20 Pa

Composition	Relative density (%)	Lattice parameter (nm) (±0.0004)	E_a ionic ($kJ\,mol^{-1}$)	
			101/21 kPa	21 kPa/20 Pa
$Ce_{0.8}Pr_{0.2}O_{2-\delta}$	92.7	0.5437	60.9	62.2
$Zr_{0.1}Ce_{0.7}Pr_{0.2}O_{2-\delta}$	96.5	0.5421	61.2	65.4