



## Chemical expansion of praseodymium-cerium oxide films at high temperatures by laser doppler vibrometry

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### A B S T R A C T

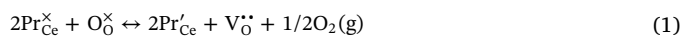
The chemical expansion of  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (PCO) films was determined as function of oxygen activity at 720 °C by laser Doppler vibrometry (LDV) in combination with previously reported chemical capacitance studies that provided relevant oxygen nonstoichiometry  $\delta$  data. The LDV method enabled detection of nanometer displacements, provided that displacement frequencies were above 1 Hz. The PCO films were deposited on yttrium stabilized zirconia (YSZ) substrates operated in the electrochemical oxygen pump mode at 720 °C to periodically adjust the oxygen activity within the PCO film. The potential across the YSZ was varied between 0 and 0.3 V, corresponding to oxygen partial pressures of about 0.2 bar and  $10^{-7}$  bar, respectively. The electrochemically induced expansion/contraction of the PCO film was observed to induce deflection in both film and substrate, as clearly demonstrated by scanning the sample surface by the LDV. A maximum displacement of about 18 nm at the center of the substrate plate was found during application of a periodic 1 Hz pumping voltage. A much lower displacement, on the order of 1 nm, was obtained when a pin-type sample support was applied, characteristic of chemical expansion of the film itself. These data were used to discuss correlations with similar recent data obtained by monitoring displacements of the PCO/YSZ sandwich structure with the aid of a specially modified nanoindenter.

### 1. Introduction

#### 1.1. Nonstoichiometry of praseodymium-cerium oxide

Nonstoichiometry in oxides governs many key materials properties including electronic and ionic conductivity, oxygen and cation diffusion, electrochemical activity in e.g. fuel cells and batteries and the response of oxide-based sensors to environmental emissions. Another key materials property, dependent on nonstoichiometry, is chemical expansion, a feature perhaps less known, that represents the degree of lattice expansion or contraction tied to a corresponding change in nonstoichiometry. Isothermal chemical expansion, like thermal expansion, must be carefully considered in the design of devices that exhibit changes in nonstoichiometry during operation to mitigate against the buildup of stresses and ultimately mechanical failure [1]. Recent studies on the chemical expansion of bulk and thin-film oxides were motivated both by potential impact on mechanical stability as well as the possibility of creating novel types of electrochemically activated high temperature actuators [2].

The praseodymium-cerium oxide solid solution system,  $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ , exhibits large deviations from stoichiometry [3] that are accompanied by chemical expansion driven by lower oxygen activities and higher temperatures [4]. Recent studies demonstrate the ability to electrochemically insert and remove oxygen reversibly from PCO films with accompanying dimensional changes [2]. Furthermore, PCO is a preferred system for investigation of chemical expansion since other properties, including its defect structure, have been previously extensively reported [3,5,6]. The following brief description of the defect model focuses on oxygen activities relevant for this work, corresponding to the oxygen partial pressure range from  $p_{\text{O}_2} = 10^{-10}$  bar to 0.2 bar. The formation of oxygen vacancies can be described by the defect relation



where  $\text{Pr}_{\text{Ce}}^{\times}$ ,  $\text{Pr}'_{\text{Ce}}$ ,  $\text{O}_{\text{O}}^{\times}$  and  $\text{V}_{\text{O}}^{\bullet\bullet}$  are  $\text{Pr}^{4+}$ ,  $\text{Pr}^{3+}$ , oxide ions and oxygen vacancies respectively. The subscripts denote the lattice sites and superscripts, the relative charge. At high  $p_{\text{O}_2}$ , Pr is largely fourfold charged. With decreasing  $p_{\text{O}_2}$  the oxidation state of Pr is reduced from

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$\text{Pr}^{4+}$  to  $\text{Pr}^{3+}$  which is compensated by the formation of oxygen vacancies (see Eq. (1)). The related defect equilibria  $K(T) \sim [\text{Pr}'_{\text{Ce}}]^2[\text{V}_{\text{O}}'']$ ,  $p_{\text{O}_2}^{1/2}$  and the approximate neutrality condition  $2[\text{V}_{\text{O}}''] = [\text{Pr}'_{\text{Ce}}] + e'$  that simplifies for sufficiently high Pr concentrations and high  $p_{\text{O}_2}$  ( $[\text{Pr}'_{\text{Ce}}] \gg e'$ ) to give the following relation between nonstoichiometry  $\delta$  and  $p_{\text{O}_2}$

$$\delta \sim 2[\text{V}_{\text{O}}''] \approx [\text{Pr}'_{\text{Ce}}] \sim p_{\text{O}_2}^{-1/6}. \quad (2)$$

This relationship describes the behavior satisfactorily, for example, down to  $p_{\text{O}_2} \approx 10^{-3}$  bar at 700 °C. Further decrease of  $p_{\text{O}_2}$  results in a smaller slope which transitions into a  $p_{\text{O}_2}$  independent plateau below  $p_{\text{O}_2} \approx 10^{-5}$  bar where the oxygen vacancy concentration is fixed by the fully reduced  $\text{Pr}^{3+}$  and continues to  $10^{-20}$  bar, far below the  $p_{\text{O}_2}$  range of interest in this study that ends at  $10^{-10}$  bar.

## 1.2. Thermo-chemical expansion of praseodymium-cerium oxide

Increases in temperature and decreases in  $p_{\text{O}_2}$  lead to expansion of PCO of up to  $\sim 1.5\%$ , significantly larger than thermal expansion by itself [7,8]. Chemical expansion, observed under an isothermal change of  $p_{\text{O}_2}$  from 1 bar to  $10^{-10}$  bar at a given temperature in the range from 650 °C to 900 °C, can be as large as  $\sim 0.4\%$ . The increase in lattice constant results from the formation of oxygen vacancies and the corresponding reduction in the valence of the Pr ions, according to Eq. (1) that is largely due to the increased Pr ion radius upon its reduction [9,10].

Such strong chemical expansion can result in stresses that lead to failure of devices, including solid oxide fuel cells (SOFCs) and oxygen permeation membranes [11]. In this context, thin films are of special interest since they enable fast operation due to short transport paths for oxygen and, simultaneously, miniaturization of devices such as high-temperature actuators. Recent investigations of thin-film PCO by nanoscale electrochemomechanical spectroscopy (NECS) clearly demonstrate chemical expansion of thin films and related effects such as substrate deflection. There, a specially modified nanoindenter was applied to investigate thin-film samples up to temperatures of 650 °C. PCO films are seen as a new class of high-temperature, non-volatile, and low-voltage electromechanical actuators [2].

In this work, a non-contacting approach is developed to investigate the chemically induced thickness changes of thin-film PCO at even higher temperatures. The applied laser Doppler vibrometer enables scanning of the sample surface that provides spatially resolved information to show e.g. substrate deflection that accompanies chemical expansion. Further objectives of this work include confirmation of stoichiometry changes of the films examined here.

## 2. Sample preparation and experimental details

### 2.1. Thin-film PCO samples

The chemical expansion of  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  films was performed using yttria stabilized zirconia (YSZ) substrates (MTI Corporation, Richmond, USA), see Fig. 1. These plates are composed of 8 mol%  $\text{Y}_2\text{O}_3$  (8YSZ) and operated in the electrochemical oxygen pump mode at  $\sim 720$  °C to periodically adjust the oxygen activity within the PCO film. Typically, the potential across the YSZ was varied by a sinusoidal voltage between  $U = 0$  and 0.3 V provided by a waveform generator. The corresponding effective  $p_{\text{O}_2}$  induced in the film is calculated to be 0.2 bar and  $10^{-7}$  bar, respectively, using the Nernst relation

$$p_{\text{O}_2, \text{eff}} = p_{\text{O}_2, \text{air}} \exp(AqU/k_B T) \quad (3)$$

where  $p_{\text{O}_2, \text{eff}}$ ,  $p_{\text{O}_2, \text{air}}$  and  $U$  are the effective  $p_{\text{O}_2}$  in the film, the ambient  $p_{\text{O}_2}$  of 0.2 bar and the applied electrical bias, respectively. A  $p_{\text{O}_2}$  of  $10^{-7}$  bar is sufficiently low to reach the  $p_{\text{O}_2}$  independent plateau mentioned in Section 1.1 provided that sufficiently fast oxygen

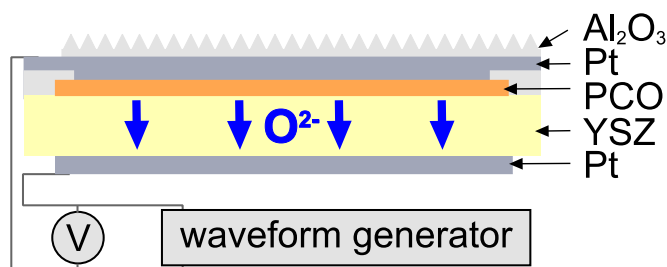


Fig. 1. PCO coated YSZ substrate with platinum electrodes and alumina capping layer for determination of chemical expansion.

transport at a given electrochemical oxygen pumping rate occurs. This issue is critical at relatively low temperatures and/or fast oxygen pumping and must be confirmed for the given experimental conditions.

The preparation of the  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  films is described in detail in [13], and, therefore, only outlined here briefly. The deposition was performed by pulsed laser deposition (PLD, Neocera Inc., Beltsville, MD) using a KrF excimer laser (Coherent COMPex Pro 205) at 248 nm with a pulse energy and repetition rate 400 mJ and 8 Hz, respectively. During deposition the substrates were heated to 725 °C and the  $p_{\text{O}_2}$  was adjusted at  $\sim 1.3 \times 10^{-5}$  bar. From wavelength dispersive X-ray spectroscopy measurements (WDS, JEOL-JXA-8200 Superprobe, JEOL, Peabody, MA), the Pr concentration at the cation sites of  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  thin films was found to be  $(9.7 \pm 0.3)\%$ , close to the nominal value of 10%. The chemical composition of an as-deposited PCO film annealed at 600 °C was investigated by means of X-ray photoelectron microscopy (XPS, Perkin-Elmer PHI-5500 ESCA Spectrometer). No specific impurity (other than carbon) was found on the as-deposited PCO film, with only peaks for carbon and oxygen obtained. Since Pr induces a very high oxygen vacancy concentration according to Eq. (1), impurities are expected to be insignificant in influencing the oxygen nonstoichiometry. The film structure was characterized by X-ray diffraction (XRD, XPert pro mpd, PANalytical). Since only {001} fluorite peaks were found, the PCO films exhibit the fluorite-structure with a predominantly (001) oriented texture. Analysis by atomic force microscopy (AFM) showed a smooth and dense layer with an apparent grain size of about 50 nm and a surface roughness of about 0.5 nm.

The deposition of the platinum front electrodes on PCO was performed by laser ablation as described in previous reports, see e.g. [5,12], respectively. The platinum back electrode on YSZ was prepared by screen printing [12]. In contrast to recent [2] and older studies [5,13], an alumina capping layer was deposited. This layer serves to decrease the oxygen leakage through the top electrode and improves, thereby, the applicability of Eq. (3) to calculate  $p_{\text{O}_2, \text{eff}}$  in the film. Further, improved optical reflectivity is achieved, necessary for effective application of the LDV.

The YSZ substrate utilized was a rectangular plate of  $10 \times 10 \text{ mm}^2$  with thickness of 0.5 mm and orientation of (100). The thicknesses of the PCO film, the platinum front electrodes, the platinum back electrode and the alumina capping layer were about 900 nm, 300 nm, 5  $\mu\text{m}$  and  $\geq 3 \mu\text{m}$ , respectively.

### 2.2. Measurement setup

The chemical expansion is determined by a specially developed setup that consists of a high-temperature furnace, interferometer and tilt mirror. Further, a camera tracks the position of the laser spot on the sample surface as visualized in Fig. 2. The components are mounted in a solid frame to minimize the impact of building vibrations. The PCO coated substrates are placed in an alumina sample holder in the gas tight tube furnace that enables operating temperatures up to 1500 °C in well defined atmospheres. For this investigation, the temperature was chosen to be 720 °C. Control of the  $p_{\text{O}_2}$  in the gas atmosphere, as for the

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