Journal of Solid State Chemistry 259 (2018) 57–66

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Strontium-free rare earth perovskite ferrites with fast oxygen exchange kinetics: Experiment and theory

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ARTICLE INFO

Keywords:
Lanthanum calcium ferrite
Praseodymium calcium ferrite
Solid oxide fuel cell cathode
Crystal structure
Defect chemistry
Oxygen exchange kinetics
Electronic conductivity
Ionic conductivity

ABSTRACT

The Sr-free mixed ionic electronic conducting perovskites $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (LCF82) and $Pr_{0.8}Ca_{0.2}FeO_{3-\delta}$ (PCF82) were synthesized via a glycine-nitrate process. Crystal structure, phase purity, and lattice constants were determined by XRD and Rietveld analysis. The oxygen exchange kinetics and the electronic conductivity were obtained from in-situ dc-conductivity relaxation experiments at 600–800 °C and $1\times10^{-3}\leq pO_2/bar\leq0.1$. Both LCF82 and PCF82 show exceptionally fast chemical surface exchange coefficients and chemical diffusion coefficients of oxygen. The oxygen nonstochiometry of LCF82 and PCF82 was determined by precision thermogravimetry. A point defect model was used to calculate the thermodynamic factors of oxygen and to estimate self-diffusion coefficients and ionic conductivities. Density Functional Theory (DFT) calculations on the crystal structure, oxygen vacancy formation as well as oxygen migration energies are in excellent agreement with the experimental values. Due to their favourable properties both LCF82 and PCF82 are of interest for applications in solid oxide fuel cell cathodes, solid oxide electrolyser cell anodes, oxygen separation membranes, catalysts, or electrochemical sensors.

1. Introduction

Perovskite-type oxides $ABO_{3-\delta}$ (with A=rare earth element or acceptor substituent, B=transition metal) represent a well-known class of mixed ionic electronic conductors which are of interest for basic research and various applications [1–3]. For instance, the air electrodes of intermediate temperature (600–800 °C) solid oxide fuel cells (SOFCs) and solid oxide electrolyser cells (SOECs) utilize (La,Sr)(Co,Fe)$O_{3-\delta}$ perovskites for the efficient conversion of the chemical energy of various fuels into electrical energy [4–6]. Recently, A-site substituted perovskite-type ferrites caused much attention due to their high ionic and electronic conductivities, their chemical stability in reducing atmospheres, relatively low thermal expansion coefficients, and their good long-term chemical stability in sulphur containing atmospheres [7–10]. The series $La_{1-x}Sr_xFeO_{3-\delta}$ (LSF) has been thoroughly studied in terms of defect chemistry [11–13], charge transport properties [14–16], and long term degradation due to different contaminants (Cr, Si, and SO_2) to test SOFC cathodes at operational conditions [17–19]. However, in order to further improve the material properties, as well as the lifespans and reliability of these compounds in technical applications, it is necessary to develop new materials with fast oxygen exchange kinetics and high thermodynamic stability. In this respect, one possible approach is to minimize the mismatch of the ionic radii of the A-site ions to prevent degradation due to mechanical stress and cation segregation [20]. The ionic radius of Sr^{2+} (XII) (1.44 Å) [21] is much larger compared to La^{3+} (XII) (1.36 Å) [21]. This can lead to the segregation of Sr towards grain boundaries and surfaces in order to relieve mechanical stress [20]. These Sr-enriched areas react with impurities from the gas phase (Cr, Si, SO_2 etc.) forming secondary phases, which inhibit the oxygen reduction process [22–24]. As a promising alternative to reduce the mismatch in the ionic radius, the smaller ion Ca^{2+} (XII) (1.34 Å) [21] can be used instead of Sr in these ferrites to obtain $La_{1-x}Ca_xFeO_{3-\delta}$. Compared to the well-characterized LSF series, only a few investigations on material properties of $La_{1-x}Ca_xFeO_{3-\delta}$ are available so far [25–33]. A study on defect chemistry, mass and charge transport properties, and oxygen exchange kinetics of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ was recently published [34], as well as an investigation on the long-term stability of $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ in SO_2 containing atmospheres [35]. Especially, only few studies on ferrite-based perovskites with varying A-site composition (other than La and Sr) are available. This is somewhat surprising, since the effects of the nature of the A-site cations on material properties have already been shown for similar solid solutions such as $Ln_{1-x}Sr_xCoO_{3-\delta}$ and $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ [36–38].

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https://doi.org/10.1016/j.jssc.2017.12.019
Received 13 September 2017; Received in revised form 13 December 2017; Accepted 15 December 2017
Available online 16 December 2017

The present study reports on the synthesis, crystal structure, defect chemistry, and various material properties (thermal expansion coefficient, electronic and ionic conductivities, oxygen surface exchange and diffusion coefficients) of the Ca-substituted ferrites $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (LCF82) and $Pr_{0.8}Ca_{0.2}FeO_{3-\delta}$ (PCF82). The influence of the A-site host cation (La^{3+} or Pr^{3+}) is investigated, while keeping the concentration of the A-site substituent (Ca^{2+}) constant. To the best of the authors' knowledge, the current paper contains the first results on the oxygen exchange kinetics of PCF82 at 600–800 °C under conditions close to equilibrium (small pO_2 gradients).

While perovskites containing La and Sr, such as $(La,Sr)(Fe,Co)O_{3-\delta}$, have been studied before by computational methods [39–41], there have been no similar investigations on the Ca or Pr containing structures. Thus, calculations on $A_{1-x}Ca_xFeO_{3-\delta}$ (A=La, Pr) were performed simulating similar Ca-content and oxygen nonstoichiometries as the experimental material to support the experiments. We compare the computed perovskite structures and their oxygen migration energies to the experimental data and include thermal effects via the harmonic oscillator approximation.

2. Experimental and computational details

2.1. Sample preparation

$La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (LCF82) and $Pr_{0.8}Ca_{0.2}FeO_{3-\delta}$ (PCF82) powders were synthesized via a sol-gel method (glycine-nitrate-process), starting with 1 M aqueous nitrate solutions prepared from $La(NO_3)_3{\cdot}6H_2O$, $Pr(NO_3)_3{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, and $Fe(NO_3)_3{\cdot}9H_2O$ (all chemicals provided by Sigma Aldrich, analytical grade quality). Stoichiometric amounts of each nitrate-solution were mixed and blended with glycine in the ratio of one mole glycine per mole cation. Similar to the process described in [34], water evaporation lead to the formation of a gel which ignited at approximately 250 °C. The resulting ash was calcined at 1000 °C and ball milled for 24 h to obtain a monomodal particle size distribution with an average particle size of 0.90 μm for LCF82, and 0.77 μm for PCF82, respectively (Fig. S-1, Supplementary material). Cylindrical pellets (length×diameter ≈ 9×5 mm) of LCF82 and PCF82 were uniaxially pressed at 5.00 kbar (maximum load 1 t), and sintered at 1100 °C for 2 h. For thermal expansion measurements, the front faces of the sintered cylinders were polished to obtain parallel ends. For conductivity relaxation experiments, as well as electrical conductivity measurements, the powders were isostatically pressed at 3.00 kbar and sintered at 1100 °C for 2 h. Sample densities were determined from the mass and geometry of the sintered pellets. Theoretical densities were obtained from Rietveld refinement (see Table S-1 Supplementary material). The density of the sintered LCF82 sample was 97% of the theoretical density (ρ_{theor}=6.3195 g cm^{-3}). The PCF82 sample exhibited 95% of the theoretical density (ρ_{theor}=6.3181 g cm^{-3}). From these dense samples, thin plates with 5×5 mm^2 cross-section and thicknesses of 200–1300 μm were prepared for measurements of the oxygen exchange kinetics and the electrical conductivity (see Section 2.3). The chemical composition of sintered LCF82 and PCF82 pellets was checked by energy dispersive X-ray spectroscopy (EDX) using an EDX Oxford Instruments detector (model 6272) in an energy range up to 20 keV (see Table S-2 Supplementary material). Three iterations on each sample were measured (neglecting oxygen), to get a good overall estimation on the cation stoichiometries. The measured values of the cation stoichiometry agree well with the theoretical values (nominal composition). Minor deviations between measured and theoretical values could be explained by the measurement uncertainty which is estimated to ± (2–3) at%.

2.2. Crystallographic and thermal analysis

X-ray diffraction (XRD) of the calcined LCF82 and PCF82 powders was performed with a diffractometer (BRUKER-AXS D8 Advance) using a Cu K α radiation source operated at 40 kV and 40 mA. The diffractograms were recorded at room temperature with a scanning rate of 0.01° s^{-1}. Lattice parameters were obtained from fitting the peak positions to an orthorhombic unit cell using the computer software MAUD [42].

The thermal expansion of LCF82 and PCF82 was measured in the temperature range of 30≤T/°C≤1000 at heating rates of 1 K min^{-1} in the oxygen partial pressure range of $1\times10^{-3}\leq pO_2/bar\leq1$, using a dilatometer (DIL 402/PC4, Netzsch). The cylindrically shaped, sintered sample was 5.1 mm in diameter and 6.9 mm in length for LCF82 and 4.9 mm in diameter and 6.8 mm in length for PCF82.

Differential scanning calorimetry (High Temperature DSC 404C Pegasus® with TASC 414/3 A controller and PU1 power unit) of the sintered LCF82 and PCF82 powder was performed in the range of 20≤T/°C≤1000 at a heating rate of 20 K min^{-1} with an isotherm at 1000 °C for 10 min and a gas flow of 50 ml min^{-1} Ar 5.0.

The oxygen nonstochiometry of LCF82 and PCF82 was determined by precision thermogravimetry (TG) using a symmetric thermobalance (Setaram model TAG 2416). Small amounts (approx. 50 mg) of the sintered powders were placed in a platinum crucible. Different oxygen partial pressures were adjusted with mass flow controllers (red-y, Vögtlin Instruments AG) using mixtures of O_2 4.5, Ar 5.0, and a test gas of 1% O_2 in Ar. An in-situ oxygen sensor with Ir/IrO_2-reference (Setnag, France) was used to determine the oxygen partial pressure close to the sample during each experiment. Experiments were performed in the isothermal and isobaric mode. The agreement between data from both experimental modes was checked, in order to confirm that all data were acquired under equilibrium conditions. Based on literature data for the similar compounds $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ [25], $La_{0.8}Sr_{0.1}FeO_{3-\delta}$ and $La_{0.75}Sr_{0.25}FeO_{3-\delta}$ [15], and $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ [43] it was assumed that $\delta \rightarrow 0$ at room temperature and pO_2=0.2 bar for LCF82 and PCF82.

2.3. Electronic conductivity and conductivity relaxation measurements

The electronic conductivity was measured as a function of temperature and pO_2 by the four-point dc van der Pauw method using a Keithley model 2400 as combined current source and voltmeter. The chemical surface exchange coefficient k_{chem} as well as the chemical diffusion coefficient of oxygen D_{chem} were obtained from in-situ four-point dc-conductivity relaxation experiments which were conducted in van der Pauw electrode configuration [44]. The dense samples had a cross section of approximately 5×5 mm^2 and were contacted with gold wires and gold paste. Platelets with two different thicknesses were used for each material, on the one hand to check the reproducibility of the data, and on the other hand to obtain both k_{chem} and D_{chem} in wider T- and pO_2-ranges. The thicknesses of the specimens were 503 and 1268 μm (LCF82) and 209 and 502 μm (PCF82). The electrical conductivity responses of the samples to step-wise changes of the oxygen partial pressure were recorded. The kinetic parameters (k_{chem} and D_{chem}) were obtained from nonlinear least squares fits of the solution of the diffusion equation to the conductivity relaxation data [11,45,46]. In order to study the oxygen exchange kinetics close to equilibrium, small pO_2-steps were performed in the oxygen partial pressure ranges 1.0×10^{-1} – 1.5×10^{-1}, 1.0×10^{-2} – 1.5×10^{-2}, and 1.0×10^{-3} – 1.5×10^{-3} bar, in oxidizing and reducing directions using O_2-Ar mixtures at a constant total gas flow of 2 dm^3 h^{-1}.

2.4. Computational details

Experimental [47] as well as computational [48] data of $(La,Sr)FeO_{3-\delta}$ indicated that a slightly different Sr-content had no effect on formation and migration energies of the oxygen vacancies. Assuming the same behaviour for Ca-containing compounds, the calculations were performed on $A_{0.75}Ca_{0.25}FeO_{3-\delta}$ (A=La, Pr) structures (indicated