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Structure and oxygen stoichiometry of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

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Abstract

High temperature X-ray diffraction (HT-XRD), temperature programmed desorption (TPD), thermogravimetric analysis–differential thermal analysis (TGA/DTA) and neutron diffraction were combined to determine the structure and oxygen stoichiometry of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) up to 1273 K in the pO₂ range of 1 to 10^{-5} atm. Formation of the vacancy-ordered brownmillerite phase, $SrCo_{0.8}Fe_{0.2}O_{2.5}$, was observed as a region of zero oxygen release in the TPD measurements and confirmed by HT-XRD and TGA/DTA. No ordering was observed in the BSCF system by any of the techniques utilized in this work. The oxygen vacancy concentration of BSCF was found to be considerably higher than that of SCF and always higher than that of the ordered brownmillerite phase of SCF, δ =0.5. The combination of a high vacancy concentration and absence of ordering leads to higher oxygen permeation fluxes through BSCF membranes in comparison to SCF. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Mixed ionic and electronic conducting (MIEC) perovskitestructured oxides are of interest as ceramic membranes for oxygen production and electrode materials for solid oxide fuel cells (SOFC). The crystal structure and oxygen defect concentration are both critical parameters influencing ionic and electronic transport, surface kinetics and mechanical properties of these materials. Oxygen separating MIEC membranes are typically subjected to oxygen partial pressures in the range 1 to 10^{-5} atm at temperatures between 973 and 1273 K. SrCo_{0.8}Fe_{0.2}O_{3- δ} (SCF) is reported to provide one of the largest membrane oxygen fluxes in the series La_{1-v}Sr_vCo_xFe_{1-x}O_{3- δ} [1–3]. However, undesirable ordering of SCF into a brownmillerite-type structure, $Sr_2Co_{1.6}Fe_{0.4}O_5$, has been reported to occur below 1073 K at pO₂ lower than around 0.1 atm [1,3–6]. This ordered state reduces the oxygen flux, while the associated lattice expansion of the membrane surface exposed to the low pO₂ side leads to large mechanical stresses across the membrane [3,7]. Recent work by Shao et al. [8,9] has demonstrated an increase in oxygen flux and an apparent increase in the stability of the cubic perovskite phase upon 50% substitution of Ba for Sr, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). In addition, BSCF has recently been proposed as a cathode material for intermediate temperature SOFC [10].

The oxygen defect concentration of perovskites is typically tuned by substituting B-site cations with more or less reducible cations or by substituting A-site cations with cations of different charge. For example, increasing substitution of Sr^{2+} for La^{3+} on the A-site of $\text{LaCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ leads to increased oxygen non-stoichiometry and, subsequently, increased ionic conductivity at the expense of stability of the cubic perovskite phase [2,11]. However, the impact on defect chemistry and vacancy ordering

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of doping the A-site with cations of the same charge is not well understood.

Various parameters have been suggested to influence the ionic conductivity in perovskite oxides. Mogensen et al. [12] suggested that lattice distortion, that is the stress caused by distortion of the perfect cubic lattice, leads to a reduction in ionic conductivity. They suggested that the A-site cation should have a radius [13] close to that of the oxide ion, 1.40 Å, implying that La^{2+} (1.36 Å) and Sr^{2+} (1.44 Å) will result in the largest ionic conductivities and that Ba^{2+} (1.61 Å) substitution will result in a reduced conductivity. However, this is in contrast with the increased membrane performance reported when Ba^{2+} is substituted for Sr^{2+} on the A-site of SCF [8]. Further factors suggested to influence the ionic conductivity of the material include the average metal-oxygen bond enthalpy and lattice free volume [14]. In comparing SCF and BSCF less than 1% difference was found in the average metal-oxygen bond energy, while the lattice free volume of both materials is below the suggested optimum of 30–35 Å³. It should be noted that both of these last parameters were suggested for solid electrolytes. Geometric influence on the ionic conductivity of the perovskite phase has also been related to the tolerance factor, *t*, with *t*=0.96 as an optimum [15]. Assuming all of the B cations in the 3+ oxidation state, δ =0.5, the tolerance factors for SCF and BSCF are 0.977 and 1.00, respectively. If we assume all of the Co in the Co²⁺ state the tolerance factors are 0.93 and 0.957, suggesting that reduction of Co³⁺ to Co²⁺ is desirable in BSCF but undesirable in SCF.

In this paper, the structure and defect chemistry of SCF and BSCF are investigated in the pO_2 range of 1 to 10^{-5} atm and between 573 and 1273 K.

2. Experimental

Phase pure commercial $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) and $Ba_{0.5-}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) powders (Praxair specialty ceramics,



Fig. 1. HT-XRD patterns of a) $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and b) $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ measured under flowing nitrogen, $pO_2 = 1 \times 10^{-3}$ atm. Higher angles are not shown for clarity.



Fig. 2. TPD oxygen, m/e=32, release spectra recorded during heating at 10 K/ min under flowing nitrogen, $pO_2=6 \times 10^{-6}$, for a) $SrCo_{0.8}Fe_{0.2}O_{2.70}$ and b) $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2.48}$ starting powders. The dashed line is the smoothed derivative of the TGA signal shown in Fig. 3a.

Woodinville, WA, USA) were annealed in air at 1373 K for 10 h before cooling at 0.5 K/min to room temperature. After grinding, the particle sizes (Mastersizer 2000, Malvern Instruments, Malvern, UK) were $d_{0.5}$ =12.0 and 16.5 µm and $d_{0.9}$ =33.9 and 36.6 µm for SCF and BSCF, respectively. The oxygen stoichiometries following this pretreatment were determined by mass change after reduction in 10% H₂/He at 1273 K for 8 h assuming SrO, BaO, Fe and Co as products.

High temperature XRD measurements (X'Pert MPD, Philips PANalytical, Almelo, The Netherlands) were made under flowing nitrogen with an oxygen concentration (Nernstian sensor, Systech Instruments, Oxford, UK) of 100 ppm with 2-h dwells at each temperature. Repeated measurements showed no change in the XRD pattern with time after one hour.

Temperature programmed desorption (TPD) measurements were made by loading 0.5 g of powder into a quartz tube packed with quartz wool. 100 ml/min STP of grade 5.0 nitrogen, with a pO_2 of 6×10^{-6} atm, was passed over the sample as the temperature was increased at 10 K/min to 1273 K. The oxygen release was monitored via a mass spectrometer (Omnistar 100, Pfeiffer Vacuum, Asslar, Germany). The sample temperature was controlled by a thermocouple wrapped around the quartz tube at the sample point. Combined TGA/DTA (Setsys, Setaram, Calurie, France) data was recorded under flowing grade 5.0 nitrogen, with a heating rate of 10 K/min.

Neutron diffraction measurements were carried out on the GEM beamline at the ISIS facility, Rutherford Appleton Laboratories, Chilton, UK. ~1.5 g of the sample powder was placed in a quartz sample holder with temperature measured with two thermocouples placed close to the sample but above the incoming neutron beam. 50 ml/min STP of calibrated gas, 100%, 10%, 1% or 0.1% oxygen in nitrogen, was supplied through a quartz capillary arranged such that the gas passed through the powder sample, causing the powder to fluidize. This ensured good mixing and decreased equilibration times. Diffraction patterns were collected while continually flushing

the sample with the calibrated gas mixture and monitoring the outlet pO_2 (Nernstian sensor, Systech Instruments, Oxford, UK). The samples were allowed to equilibrate, determined as no change in lattice constant, at 600 °C before measurement during temperature ramps, 1.33 K/min, in each gas environment. Oxygen stoichiometries were extracted by refining the lattice occupancy of oxygen during Rietveld refinement [16] using the GSAS suite of programs [17]. A detailed discussion of these measurements will be presented elsewhere [18,19].

3. Results

Room temperature XRD patterns of both SCF and BSCF could be indexed using a cubic perovskite unit cell, space group Pm-3m, after the air pretreatment. High temperature XRD measurements were carried out under both air and flowing nitrogen atmospheres. Under air both SCF and BSCF maintained a cubic perovskite structure over the temperature range 573 to 1273 K. Fig. 1a, shows the HT-XRD patterns measured for SCF under flowing nitrogen. At 573 K, the equilibrium pattern shows orthorhombic symmetry associated with the formation of the brownmillerite-type structure, $Sr_2Co_{1.6}Fe_{0.4}O_5$. Between 973 and 1073 K the oxygen vacancies disorder and cubic symmetry is restored. In contrast to this, BSCF, Fig. 1b, shows a cubic, vacancy disordered structure under nitrogen over the entire temperature range.



Fig. 3. TGA/DTA spectra recorded during heating at 10 K/min under flowing nitrogen, $pO_2=6\times10^{-6}$, for a) $SrCo_{0.8}Fe_{0.2}O_{2.70}$ and b) $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2-0}O_{2.48}$ starting powders.



Fig. 4. Oxygen stoichiometry as a function of temperature for BSCF (open symbols) determined by neutron diffraction at pO_2 of a) 1, b) 0.1, c) 0.01 and d) 1×10^{-3} atm. Data for SCF (closed symbols) determined by gravimetric methods (5) are provided for comparison measured at pO_2 of a) 1, b) 0.102, c) 0.015 and d) 5×10^{-4} atm. Dashed lines are provided as a guide to the eye.

Temperature programmed desorption was employed to further probe the oxygen release characteristics of these materials. After an initial oxygen release peak starting at 575 K, the oxygen release rate from SCF decreases rapidly and the m/e=32 signal falls to the baseline, Fig. 2a. Above 1050 K, significant oxygen release recommences. The BSCF TPD profile, Fig. 2b, shows an initial oxygen release coincident with that of SCF suggesting that the release kinetics of the two samples are similar. However, in contrast to SCF, the oxygen release from BSCF is continuous up to the maximum temperature probed, 1273 K.

TGA/DTA measurements were performed in order to accurately measure the oxygen nonstoichiometry and confirm the occurrence of possible order-disorder transitions in these materials. The initial oxygen stoichiometries were found to be 2.70 and 2.48 for SCF and BSCF, respectively. 2.70 for SCF cooled in air is in good agreement with the literature value of 2.754 for SCF cooled in pure oxygen [5]. The small difference is attributable to the difference in pO_2 during cooling. Note that the oxygen stoichiometry of BSCF is considerably lower than that of SCF. The TGA/DTA data is analogous to that collected by TPD in that the TPD data corresponds to the derivative of the TGA signal. This is confirmed in Fig. 1a where the dashed line shows the numerical derivative of the TGA signal coincident with the TPD profile of SCF, although there is a 15 K temperature discrepancy in the initial peak maximum. This may be explained by differences in thermocouple location, furnace

system and gas flow between the two experiments. As with the TPD data, no change in oxygen stoichiometry was observed below 575 K. Above this temperature the oxygen stoichiometry of SCF, Fig. 3a, rapidly decreases to 2.5 where it becomes constant until a phase change, confirmed by a large endotherm, that is the peak in the DTA signal, occurs at 1050 K. This internal reference, the plateau in oxygen stoichiometry associated with the brownmillerite phase, provides further confirmation of the initial oxygen stoichiometry determined by reduction in H₂. Above 1050 K, the oxygen stoichiometry decreases to 2.43 at 1273 K. The initial oxygen stoichiometry of BSCF is significantly lower than that of SCF and below that associated with the brownmillerite structure, 2.5. Fig. 3b shows that the stoichiometry decreases further to a final value of 2.24 at 1273 K with no significant departure from the background DTA signal, confirming that BSCF does not undergo a phase transition in this region. The samples were allowed to equilibrate at 1273 K under N2 until constant mass, yielding equilibrium oxygen stoichiometries of 2.36 and 2.18 for SCF and BSCF, respectively.

Neutron diffraction experiments were performed in order to measure both the equilibrium oxygen stoichiometry and structure of BSCF simultaneously as a function of oxygen partial pressure and temperature. The oxygen stoichiometry of BSCF is determined directly from structural refinement of the neutron diffraction data and is therefore independent of the stoichiometry determined by reduction in H₂ [18,19]. Fig. 4

shows the equilibrium oxygen stoichiometry of BSCF plotted versus temperature for four different oxygen partial pressures, 1, 0.1, 0.01 and 0.001 atm. Literature data [5] for SCF are provided for comparison. The cubic perovskite structure, space group Pm-3m, was observed for BSCF at all oxygen pressures and temperatures measured. The maximum values for RWP, RP and χ^2 for all the data presented here were 3.4%, 3.3% and 1.35, respectively. There is some scatter in the determined oxygen stoichiometries due to time restrictions requiring limitation of the counting time. However, a smooth decrease in oxygen stoichiometry with temperature at each oxygen pressure is observed. The oxygen stoichiometries measured by neutron diffraction are in relatively good agreement with those calculated from the TGA results. It should be noted that due to the fast temperature ramp, the sample in the TGA is not completely at equilibrium resulting in increased oxygen stoichiometry in the TGA data in comparison to those determined by neutron diffraction.

4. Discussion

It is important to consider both the sample pre-treatment and experimental procedure when discussing the TPD results. As the samples were pretreated in air and transferred to a low pO₂ environment at room temperature, the oxygen stoichiometry of the lattice is far from equilibrium with the gas phase. This results in a large thermodynamic driving force for oxygen release at the beginning of the TPD experiment. At low temperatures slow kinetics prevents release of oxygen. This kinetically trapped oxygen is termed non-equilibrium oxygen in the following discussion. In the temperature programmed experiments presented here, the kinetics do not become sufficiently fast until 575 K, where the non-equilibrium oxygen is released as a large single peak in the TPD profile. The position of this kinetically dominated peak is determined by sample particle size and heating rate. Since particles with a $d_{0.9}$ of $\sim 35 \,\mu m$ were used, that is, with characteristic length less than the critical thickness criterion [20], it is expected that surface kinetics dominate the low temperature release of oxygen. Beyond this surface-limited region, the particles rapidly equilibrate with the gas phase and we observe oxygen release closer to the equilibrium behavior.

As confirmed by TGA measurements, the zero release region of the SCF profile is associated with the formation of the brownmillerite structure at an oxygen stoichiometry of 2.5. That is the thermodynamic equilibrium oxygen stoichiometry at this temperature and pO_2 . No further significant oxygen release occurs until the structure disorders above 1050 K, coinciding with the second high temperature oxygen release observed by TPD and TGA and in agreement with XRD measurements, Fig. 1a. These changes in structure and oxygen stoichiometry agree with a recent study utilizing in situ neutron diffraction [21].

Evidence that the lower temperature, non-equilibrium oxygen release peak of SCF is dominated by kinetics is confirmed by the XRD measurements, Fig. 1a. The brownmillerite phase of SCF is fully developed in the XRD measurement made at 573 K; however, this does not form until 750 K in the temperature programmed measurements. The difference is due to the use of a rapid temperature ramp in the TPD and TGA–DTA experiments and slow equilibration in the XRD. The continual release of oxygen in the TPD profile of BSCF is associated with the lack of an order–disorder transition in BSCF.

The changes in B-cation oxidation state associated with the oxygen release peaks in the TPD profile may be deduced from the oxygen stoichiometry data. For SCF, approximately 40% of B cations are initially in the 4+ oxidation state, and the initial peak is associated with reduction of B^{4+} to B^{3+} . The SCF system orders when the average B-cation oxidation state is 3+, corresponding to an oxygen stoichiometry of 2.5. The second release peak for SCF is associated with the further reduction from B^{3+} to B^{2+} and is coincident with the order-disorder transition. TPD and TGA measurements indicate that this coincides with Co3+ and Co2+ reduction in similar materials, suggesting that the order-disorder transition in SCF is driven by the further reduction of Co. In contrast to SCF, the initial average oxidation state of B cations is less 3+ in BSCF in conflict with the previous assignment of the low temperature transition peak to the reduction of Co^{4+} to Co^{3+} . We suggest that the position of the low temperature peak in the TPD profile is primarily related to kinetic effects, as outline above. As with SCF, we suggest that further reduction of oxygen stoichiometry occurs primarily through reduction of Co^{3+} to Co^{2+} as Fe^{3+} is more stable in this $T-pO_2$ region. This assumption is in agreement with the final oxidation state of BSCF, close to the 2.1 expected for average B-cation oxidation states of Co^{2+} and Fe^{3+} . The enhanced reduction of Co³⁺ shifts the tolerance factor for BSCF closer to the suggested optimum of 0.96 [15].

Increased basicity of the A-cation is expected to stabilize higher oxidation states of the B cation. From this it was expected that doping with Ba^{2+} , which is more basic that Sr^{2+} , would lead to higher oxygen stoichiometries. However, the oxygen stoichiometry of BSCF is significantly lower than SCF over the entire $T-pO_2$ region considered in this study. It is concluded that Ba-doping on the A-site decreases the stability of higher oxidation states of the B-cations. One possible explanation is the increased lattice constant, and therefore increased average metal-oxygen bond distance, occurring when the larger Ba^{2+} cation is substituted for Sr^{2+} . At room temperature the A-O and B-O bond distances determined by neutron diffraction [18,19] increase from 2.739 to 2.823 and 1.936 to 1.996 for SCF and BSCF, respectively. This increased bond distance will decrease the electron density around the Bcation, leading to lower average oxidation state. However, the oxygen stoichiometry of BSCF at these conditions is lower than that of SCF, leading to lattice expansion and making it difficult to extract cause from effect.

Even at room temperature, the oxygen stoichiometry of BSCF is below that of the vacancy ordered brownmillerite phase. However, ordering may occur in perovskite oxides at lower oxygen stoichiometries of 2.33, 2.25 and 2.0 [21]. We suggest that ordering does not occur in BSCF as the presence of mixed A-site cations disrupts the uniform A-site periodic potential required to form ordered structures. The brownmillerite

phase occurs in SCF in a uniform lattice with only one A-site cation and both Co and Fe in the 3+ oxidation state.

In terms of the targeted membrane and electrode applications, coupling the low oxygen stoichiometry of BSCF with maintaining the cubic perovskite structure leads to a high concentration of mobile oxygen vacancies and a high oxygen ion conductivity [22]. At low temperatures, ordering in SCF reduces the oxygen flux in comparison to BSCF [3]. At higher temperatures, where both materials show cubic symmetry, the higher vacancy concentration of BSCF may be the reason for the reported increased oxygen flux [8]. Finally, the formation of ordered phases at the low pO2 side of SCF membranes is expected to lead to large chemical expansion coefficients [7]. With no phase transition, the stresses developed in an operating BSCF membrane are expected to be considerably lower. However, the lowest oxygen stoichiometry measured, 2.18 at 1273 K, $pO_2 = 6 \times 10^{-6}$ atm, suggests that these conditions are close to the stability limit of the material.

5. Conclusion

Temperature programmed techniques yield useful insights into the oxygen stoichiometry of perovskite-structured oxides. Substitution of Ba²⁺ for Sr²⁺ on the A site of SCF leads to a significant increase in oxygen non-stoichiometry up to 1273 K at pO_2 values between 1 and 10^{-5} atm. The oxygen stoichiometry is below that of the ordered brownmillerite phase of SCF. BSCF maintains cubic symmetry at all temperatures and oxygen partial pressures covered by the present experiments. The combined influence of low oxygen stoichiometry and cubic structure is the likely cause of increased oxygen permeation fluxes through BSCF membranes compared with SCF.

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