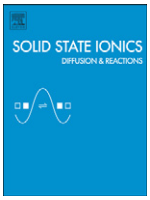
Solid State Ionics 197 (2011) 25–31

Contents lists available at ScienceDirect

Solid State Ionics

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



Thermal stability of the cubic phase in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)1

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ARTICLE INFO

Article history:
Received 9 March 2011
Received in revised form 18 May 2011
Accepted 15 June 2011
Available online 27 July 2011

Keywords:
BSCF
Electrical conductivity
Phase stability
Hexagonal phase

ABSTRACT

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is a material with excellent oxygen ionic and electronic transport properties reported by many research groups. In its cubic phase, this mixed ionic-electronic conducting (MIEC) perovskite is a promising candidate for oxygen permeation membranes. For this application, its long-term stability under operating conditions (especially temperature and oxygen partial pressure) is of crucial importance.

The present work is focused on the thermal stability of the BSCF cubic phase in the targeted temperature range for applications (700…900 °C) in light of previous studies in literature reporting a reversible transition to a hexagonal phase somewhere below 900 °C.

To this end, single phase cubic BSCF powders were annealed at different temperatures over varying periods of time. Phase composition was subsequently analysed by X-ray diffractometry (XRD) in order to determine both the temperature limit and the time-scale for the formation of the hexagonal phase. Additionally, the long-term behaviour of the electrical conductivity was examined on bulk samples at 700 °C, 800 °C and 900 °C over several hundreds of hours, showing a prolonged decrease at 800 °C. The decrease in electrical conductivity at this temperature was also examined on bulk samples with different grain sizes, showing a more pronounced decrease the smaller the average grain size.

Coexistence of both phases (cubic and hexagonal) could also be shown for 700 °C, however with a different phase equilibrium than at 800 °C.

1. Introduction

For an application as dense high-temperature oxygen-transport membranes (OTM), mixed ionic-electronic conducting (MIEC) metal oxides are of great interest, given their excellent transport properties, resulting in both high oxygen permeability and selectivity for oxygen/air separation in the targeted temperature range (~800 °C) [1]. Amongst the most promising oxides are those of the perovskite (ABO_3) type, a structure that combines great flexibility and chemical stability, thus permitting custom-tailoring of the materials properties by doping the A or B sites with different elements and stoichiometries. In this structure, electronic conductivity is provided by at least one multivalent metal ion in the B-site of the perovskite, consequently the electrons are able to hop between the metal ions. In order to obtain oxygen conductivity, it is possible to partially or totally substitute the A^{3+} metal ion in the A-site of the perovskite by alkaline earth cations, such as Sr^{2+}. By means of charge compensation, this leads to a high concentration of oxygen vacancies $[V_O^{\cdot\cdot}]$ in the anionic sublattice, origin of the oxygen ionic conductivity.

In the case of the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) perovskite, its very high oxygen permeation fluxes reported in the literature [2–4] have been attributed to its large vacancy concentration. However, SCF is only stable at high temperatures and oxygen partial pressures, whilst it is transformed to a vacancy-ordered brownmillerite, with low oxygen conductivity, at temperatures below 790 °C [5]. Shao et al. [6,7] could improve the stability of SCF and avoid the formation of the brownmillerite phase by substituting the A-site of the perovskite with the larger size cation Ba^{2+}. In doing so, they also observed a slight increase in its permeation rate. In this way, the composition $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (henceforth denoted as BSCF) was found to exhibit outstanding oxygen permeation fluxes (see, e.g., [6–9]). Initially, BSCF was presented to show very promising performance as a prospective cathode material for intermediate-temperature solid oxide fuel cells (SOFC) as well [10].

These findings have stimulated research on this particular materials composition in recent years; an overview is given by [11]. Many

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doi:10.1016/j.ssi.2011.06.010

research groups have investigated the electrochemical properties of BSCF by studies of the electrical conductivity of BSCF ceramic bulk samples [12–15], application of conductivity relaxation techniques on BSCF bulk samples [16–18] and thin films [19] as well as oxygen tracer diffusion in thin films [20] and powder samples [21] thus yielding a basic set of parameters concerning the oxygen transport properties of BSCF which can be considered superior, as compared to other state-of-the-art perovskites, e.g. $(La,Sr)(Co,Fe)O_{3-\delta}$.

However, there has been surprisingly little knowledge about the long-term structural and electrochemical stability of BSCF under application-relevant temperatures. Even though it is well-known that BSCF is not stable when operated in atmospheres containing carbon dioxide due to the formation of carbonates [22–25] – a fact putting a question mark on the applicability of BSCF cathodes for SOFC operation in ambient air – little has been reported on the structural stability of the cubic perovskite phase in BSCF, notably on the temperature-phase relationship, until recently.

A slow exponential decrease of the oxygen permeation rate with time (over ~400 h), caused by a phase transition, was already reported by Shao et al. [7] when BSCF membranes were operated at temperatures below 825…850 °C, and more recently, e.g., by Efimov et al. [26] at 750 °C. It has been observed that the cubic perovskite phase is not stable in air below these temperatures; a reversible phase change from a cubic into a two-phase mixture of hexagonal and cubic perovskites occurs [27]. According to Arnold et al. [28], this change would take place via a new monoclinic perovskite.

Recently, there have been several further accounts in literature reporting on the phase composition of BSCF in the intermediate temperature range (around 800 °C). D. Müller et al. [29] were able to analyse the formation kinetics of the hexagonal BSCF phase at 800 °C by a combined XRD/electron microscopy study, resulting in a detected phase equilibrium between hexagonal and cubic perovskite phase at temperatures of 800 °C. By means of TEM analysis P. Müller et al. [30] reported on a yet not unambiguously identified phase present in BSCF at intermediate temperatures, beside the expected cubic and hexagonal polymorphs. Efimov et al. [31] very recently presented a detailed TEM study, identifying a decomposition of cubic BSCF into not only the hexagonal but also further phases in the intermediate temperature range below ~850 °C.

As the oxygen-transport properties, especially on a long-term time scale, are very sensitive to changes in material and/or phase composition, investigations concerning the phase stability of BSCF and the corresponding transport properties, are highly anticipated, thus addressing issues of further performance optimization in the operating temperature range (700…900 °C).

2. Experimental

2.1. Sample preparation

2.1.1. Powders

Commercially available $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) powders prepared by mixed-oxide route were provided by the Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Hermsdorf/Germany. The D_{50} value of the powder was determined by particle sizer analysis (CILAS 1064L) to be at around 2.40 µm.

XRD analysis (see graph (a) in Fig. 3) showed the powder to be of the single phase cubic perovskite structure with a lattice constant of 3.986 Å, which corresponds well to the values determined by other groups, e.g. [27] and [32]. All nine reflections in the 2Θ-range from 20° to 80° have been fitted using WinINDEX (Bruker AXS) and yielding only one possible result.

Annealing of the BSCF powders in ambient air was done using chamber furnaces, whilst treatment in synthetic air was performed in a tube furnace with a mixture of 20% oxygen in nitrogen. Heating and cooling rates have been fixed to 20 K/min.

2.1.2. Bulks

From the single-phase cubic BSCF raw powders, bulk samples were prepared by uniaxial pressing at ca. 10 kN/cm² and sintering for 12 h at 1000 °C, for 50 h at 1120 °C and 50 h at 1150 °C (heating and cooling rates 5 K/min), resulting in mean grain sizes around 25 µm, 50 µm and 90 µm, respectively, as determined by analysis using the software SPIP (Image Metrology A/S, Denmark). These bulks were subsequently cut by ultrasonic lapping and mechanically polished (P1200 emery paper), yielding bulk samples with a geometry of $10\times5\times0.4\ mm^3$ and $10\times5\times1\ mm^3$.

For conductivity measurements the bulks were contacted with Pt wires using a frit-free Pt paste fired at 1100 °C for 1 h in ambient air. Owing to the fairly low electrical resistance of the BSCF bulks, electrical measurements were carried out in 4-point technique (cf. Section 2.3).

2.2. Structural characterization

Pre-test and all further X-ray diffractometrical (XRD) analyses on powders and bulks were carried out using a Siemens D-5000 spectrometer (Bruker-AXS, Karlsruhe, Germany) with CuK_α radiation and a scintillation detector. All measurements were done in a 2Θ-range from 20° to 80° with a current and voltage of 40 mA and 40 kV respectively, step size was set to 0.01° with a scan speed of 10 s per step in the locked coupled mode and a variable slit (V20) for both divergence and antiscatter slit as well as a Ni filter with a thickness of 0.2 mm in front of the detector.

All spectra have been corrected for $CuK_{\alpha2}$-radiation, and the background has been subtracted, using the programme EVA (Bruker AXS).

2.3. Conductivity measurements

Long-term conductivity measurements in ambient air have been conducted on the BSCF bulks in a chamber furnace. In this setup, five four-wire contacted samples can be measured at the same time by applying a serial current using a Keithley 224 programmable current source whilst sequentially reading the voltage over each sample's contacts using a Keithley 2000 multimeter. A possible sample degradation over time due to ionic demixing as a result of long-term DC loading could be ruled out by a careful comparison of long-term measurements on the same set of samples, one with a continuous current, the other with a setup that only applied a measurement current for one minute every hour to get a set of data points. Both experiments yielded the same rate of degradation, ruling out kinetic demixing as reason for this behaviour. Given the fairly high conductivity of BSCF and the resulting small electric fields in the sample, this was to be expected.

3. Results and discussion

3.1. Long term conductivity measurements

The grey curve in Fig. 1 shows the conductivity of a BSCF bulk sample measured in ambient air over several hundred hours each at temperatures varying from initial 900 °C over 800 °C to finally 700 °C. The different behaviour of the conductivity as a function of time at these three temperatures will be discussed below. First, however, the conductivity data have to be normalised.

Due to the highly changeable oxygen nonstoichiometry of the BSCF lattice at these high temperatures, resulting in substantial oxygen exchange with the ambient gas phase:

$$^{1}/_{2}O_{2,gas} + V_{O}^{\cdot\cdot} \rightleftharpoons O_{O}^{x} + 2h^{\cdot} \quad (1)$$