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Original Article

Yttrium doping of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ part I: Influence on oxygen permeation, electrical properties, reductive stability, and lattice parameters

Lana-Simone Unger^{a,*}, Christian Niedrig^a, Stefan F. Wagner^a, Wolfgang Menesklou^a,
Stefan Baumann^b, Wilhelm A. Meulenberg^b, Ellen Ivers-Tiffée^a

^a Institute for Applied Materials – Electrical and Electronic Engineering (IAM-WET), Karlsruhe Institute of Technology (KIT), 76131, Karlsruhe, Germany

^b Institute of Energy and Climate Research – Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, 52425, Jülich, Germany

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ABSTRACT

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) exhibits a very high oxygen permeability in its cubic perovskite phase, making it a promising candidate for high-temperature energy-related applications such as oxygen-transport membranes. It suffers, however, from a pronounced phase instability at application-relevant temperatures below 840 °C which is presumed to result from a valence change of B-site cobalt. In an attempt to stabilize the cubic BSCF phase, monovalent Y^{3+} was doped in small concentrations (1–10 mol-% yttrium) onto its B-site. The influence of this doping on the physico-chemical properties (electrical conductivity, reductive stability, lattice constant), on the sintering behavior, and on the oxygen permeation of BSCF has been systematically investigated. Despite a slightly adverse effect to permeability (decrease in oxygen permeation by about 20–30%), a doping concentration of 10 mol-% Y is found to completely suppress secondary-phase formation and, hence, stabilize the cubic BSCF system at 800 °C. These findings are extremely promising with regard to a long-term operation of BSCF in atmospheres free of acidic impurity gases.

1. Introduction

There is an existing demand for pure oxygen in a variety of industrial processes that is currently being met by the well-established fractional distillation of liquefied air. This cryogenic method, however, is a highly energy-intensive process. A significantly more efficient alternative separates oxygen from pressurized air at elevated temperatures using solid-state membranes, thus opening up a range of new applications such as in CO_2 -neutral power plants [1,2] or an integration in catalytic membrane reactors for various chemical processes [3]. Such a dense gas-tight membrane, composed of a mixed ionic-electronic conducting (MIEC) material, facilitates ambipolar oxygen transport (without any need for additional electrode layers) through the solid state and is ideally 100% selective with regard to O_2 separation from a gaseous mixture of oxygen and N_2 (plus potential contaminants, such as in power-plant environments typically CO_2 , SO_x ...). Using single-phase MIEC materials, high oxygen fluxes are often obtainable. Under atmospheres containing contaminants such as CO_2 , however, several alternative concepts involving dual-phase materials (composite membranes) show promise, e.g., [4,5]. Since the seminal work of Teraoka et al. [6,7] on the remarkable transport properties of selected mixed ionic-

electronic conducting (MIEC) perovskite-type oxides thirty years ago, several chemical compositions based on the formula $\text{A}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (with $\text{A} = \text{La}, \text{Ba}, \text{Pr}, \dots$) have attracted great interest for selected high-temperature applications, especially in the energy-related sector. Their high degree of oxygen permeability at elevated temperatures (typically within the range from 600–900 °C), which relates both to a high amount and mobility of oxygen vacancies as well as a sufficient electronic conductivity, has destined them as materials suitable for, e.g., solid oxide fuel cell (SOFC) cathodes [8,9] or oxygen-transport membranes [3,10].

As the remarkable flexibility exhibited by the perovskite ABO_3 structure with respect to cation substitution has facilitated a highly convenient custom-tailoring of material properties, several MIEC oxides have emerged over the past three decades with particular promising oxygen-transport properties. Most notably, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) was proposed by Shao et al. [11,12] and has since emerged as a composition with an outstanding oxygen permeation flux [13]. It has been a materials advancement on its well-performing cubic-perovskite “predecessor” $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) [6,14–16] which suffered from a phase transition to an orthorhombic brownmillerite structure owing to an ordering of oxygen vacancies [16,17]. Since this led to a decrease of

* Corresponding author at: Karlsruhe Institute of Technology (KIT), Institute for Applied Materials – Electrical and Electronic Engineering (IAM-WET), Adenauerring 20 b, 76131 Karlsruhe, Germany.

E-mail address: [lana.unger@kit.edu](mailto: lana.unger@kit.edu) (L.-S. Unger).

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oxygen-vacancy mobility, several attempts were made at improving the structural stability of the cubic perovskite phase, and the addition of A-site barium (BSCF) turned out to be optimal not only with respect to stabilization, but also with respect to oxygen permeability [11]. Due to the large non-stoichiometry in the anion sublattice [18], transport of oxygen ions via vacancy sites is promoted, and due to multivalent B-site cations, in particular cobalt, electron hopping provides electronic conductivity.

Moreover, BSCF could recently be shown to be chemically stable even in reducing atmospheres down to an oxygen partial pressure pO_2 of (at least) 10^{-10} bar at 900 °C [19–23].

Even though an application of BSCF for, e.g., SOFC cathodes severely suffers from a very limited chemical stability against even small amounts of acidic contaminants such as, e.g., CO_2 [24–27] that inevitably may occur in technical processes, an OTM operation in CO_2 -free atmospheres, such as oxyfuel combustion in three-end mode [2,28], is conceivable that does not present any problems with respect to carbonation and thus makes BSCF a promising material of choice. However, one prerequisite for such a long-term operation is a sufficient material stability over a period of several years at operating temperatures of 700–900 °C.

It was previously shown that BSCF forms several secondary phases at temperatures below 900 °C that lead to a degradation of oxygen-transport properties, as compared to those of the cubic BSCF phase. It is safe to assume that the oxygen permeability of a polycrystalline BSCF membrane is very sensitive to the occurrence of non-cubic secondary phases in the application-relevant temperature and partial-pressure range. This is presumably due to the valence state of the B-site cobalt ion that has been determined to range between +2.2 (cubic BSCF) and +2.8 (hexagonal BSCF) [29], leading to a decrease of its ionic radius for the higher valence state and, hence, to an increase of the Goldschmidt tolerance factor above unity which ultimately results in a destabilization of the cubic perovskite structure owing to steric effects [29].

Švarcová et al. [30] were the first to analyze the formation of a hexagonal secondary phase in BSCF, which was later shown to be iron-deficient [31,32], at below 850–900 °C. The occurrence of cobalt-oxide precipitates was also reported in literature [33–35]. Further work by Müller et al. [36,37] found additional segregation of a “plate-like” phase consisting of a stacking of nanoscaled lamellae of hexagonal, cubic and a BCO-type ($Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$ ($n \geq 2$)) phase, which in itself consists of a sequence of CdI_2 -type layers and perovskite layers [37,38]. Moreover, it could be shown that while the electric conductivity of dense ceramic BSCF bulk samples remains constant over several hundred hours at $T = 900$ °C, a pronounced degradation of 3% over a time period of 860 h could be observed at $T \leq 840$ °C [39].

All in all, a severe degradation of the oxygen-permeation properties at temperatures below 900 °C, already observed, e.g., by Shao et al. in 2000 [11], could be related to the partial decomposition of the cubic BSCF phase. In view of the remarkable oxygen-transport kinetics exhibited by cubic BSCF, its lattice instability is not too surprising; Kuklja et al. [40] in fact ascribe both phenomena to the same mechanistic origin, in particular the substantial size mismatch between A- and B-site cations in BSCF of the present stoichiometry.

Many groups have therefore recently aimed at a specific materials engineering of the BSCF system in order to stabilize its cubic phase, at least within a certain application-relevant temperature range. As cobalt was identified as a culprit in the destabilization of the cubic phase, several attempts have aimed at substituting Co completely, for instance using Al, Cu or Zn instead [41–44]. While these studies showed an increased phase stability of the cubic perovskite, this was, however, achieved at the expense of a considerable decrease in oxygen permeability. Alternative approaches have aimed at a partial substitution of B-site ions by suitable other cations, i.e. redox-stable cations with high valence ≥ 3 , such as yttrium [45–49], zirconium [50–52], niobium [53,54], or antimony [55]. In any case, controlling the cobalt valence

was identified as the key factor for stabilization of cubic BSCF. Whereas some of these attempts have failed to show unambiguous results with respect to phase stabilization and, thus, were not able to completely prevent long-term degradation of electrochemical transport properties within a desired thermal window of operation (e.g., temperatures of around 800 °C), yttrium B-site doping has shown great promise given preliminary results by Haworth et al. [45–47,56] and own previous studies focusing on microstructural analyses [35].

In the present study, focus is therefore laid on the role of Y doping in BSCF. As yttrium cations have a higher ionic radius as compared to cobalt [57] and, furthermore, remain monovalent, it is to be expected that a partial substitution of the smaller Co^{3+} cations (with their ionic radius of ~ 55 pm) with Y^{3+} cations (with an ionic radius of ~ 90 pm) should be able to counteract the phase transformation from cubic to hexagonal and, thus, noticeably contribute to a stabilization of the cubic phase in the BSCF matrix [48,49].

To this end, a systematic analysis of the influence of B-site yttrium doping at varied doping levels (0–10 mol-% B-site concentration) on the performance of BSCF has been carried out. This includes the permeation properties of the BSCF matrix with Y doping between 650–1000 °C as well as long-term measurements and its electrical properties both as a function of temperature T (between 25–900 °C) and oxygen partial pressure pO_2 (between air and 10^{-4} bar). Furthermore, chemical stability at high temperatures ($T = 950$ °C) under reducing conditions ($10^{-14} \leq pO_2/\text{bar} \leq 0.21$) and changes in the lattice constant and the resulting thermal and chemical expansion behavior (both in synthetic air and in nitrogen, between 25–900 °C) were studied.

In a second paper [58], closely related to the present study, the influence of the yttrium content of BSCF on its phase composition in the temperature range between 640–1100 °C and on its oxygen-transport kinetics at 700 and 800 °C, respectively, have been studied. From the combined experimental results, the influence of Y doping on the stabilization and electrochemical performance of the BSCF matrix can be comprehensively assessed.

2. Experimental

2.1. Sample preparation

Powders of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and B-site cation-substituted $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Y_xO_{3-\delta}$ (henceforth referred to as BSCF:100xY), with $x = 0, 0.01, 0.03$ and 0.10 , were prepared by mixed-oxide route, using $BaCO_3$ (Merck KGaA, Darmstadt, Germany, SelectipurTM, particle size 1 μm), $SrCO_3$ (Merck KGaA, Darmstadt, Germany, TechnipurTM, particle size 1 μm), Co_3O_4 (chemPUR, Karlsruhe, Germany, 99.9756% purity, particle size 4 μm), Fe_2O_3 (Alfa Aesar, Karlsruhe, Germany, 99.5% purity, particle size 500 nm), and Y_2O_3 (Alfa Aesar, Karlsruhe, Germany, 99.99% purity, particle size 4 μm) as starting materials. Multiple grinding and calcination steps were carried out to achieve homogeneous powders. Grinding of educts was carried out in a ball mill (2–20 h) in order to obtain a homogeneous particle size of ~ 500 nm (BSCF) and ~ 300 nm in the case of the dopant Y. Calcination was carried out in two steps: in the case of BSCF, BSCF:1Y, and BSCF:3Y, at a temperature of 900 °C (2 h dwell time for the first step, after subsequent cooling and grinding in a mortar 4 h further dwell time for the second step, heating and cooling rates for all steps 2 K min^{-1}), in the case of BSCF:10Y the same procedure at a calcination temperature of 950 °C. The calcined powders were finally ground in a ball mill for 24 h. The D_{50} value of the powders after milling was determined by particle sizer analysis (CILAS 1064L, Orléans, France) to be around 2 μm , and the single phase cubic perovskite structure was confirmed by X-ray diffraction (XRD) analyses (2.2)

The raw powders were granulated prior to uniaxial pressing at ca. 10 kN cm^{-2} into dense samples (bar-shaped bulks for electrical conductivity measurements, round disks for XRD analyses and oxygen permeation measurements). The green density of the pressed samples

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