



Decomposition pathway of cubic $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ between 700 °C and 1000 °C analyzed by electron microscopic techniques

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ARTICLE INFO

Article history:

Received 31 May 2011

Received in revised form 9 September 2011

Accepted 11 October 2011

Available online 12 November 2011

Keywords:

BSCF

Transmission electron microscopy

Perovskites

Phase stability

Mixed conductor

ABSTRACT

Mixed ionic–electronic conductors and, among those, in particular $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) with high oxygen ion conductivity are of great interest for oxygen separation membranes. To study the decomposition of BSCF5582 under application-relevant conditions, BSCF5582 bulk samples were annealed at temperatures between 700 °C and 1000 °C and investigated by X-ray diffractometry and various electron microscopic techniques. Beside the verification of the formation of a hexagonal phase, an additional phase with plate-like morphology and trigonal crystal structure is observed. While the crystallization of the hexagonal phase is limited to temperatures below 830 °C, the plate-like phase is detected up to 900 °C annealing. The chemical composition of the hexagonal and plate-like phases was analyzed by energy dispersive X-ray spectroscopy. The plate-like phase is characterized by a cobalt enrichment and strontium depletion whereas the barium concentration remains unchanged with respect to the cubic BSCF matrix. The kinetics of the decomposition at 800 °C of the cubic phase was studied by annealing treatments up to 1350 h. The plate-like phase shows fast precipitation whereas the formation of the hexagonal phase was found to be significantly slower.

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1. Introduction

The reduction of CO₂ emission of coal or gas power plants has gained increasing attention in recent years. One approach to achieve a significant reduction of CO₂ emission is the application of sophisticated new materials for the fabrication of oxygen separation membranes with high efficiency and oxygen selectivity. This field was reviewed comprehensively by Bouwmeester and Liu [1,2]. Promising materials for the application as oxygen separation membranes are mixed ionic–electronic conducting perovskites as reported by several groups [3–7]. Teraoka for instance developed high oxygen-flux separation membranes on the basis of the $\text{SrCo}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (SCF) system [8]. This material is characterized by a high concentration of oxygen vacancies due to Sr²⁺ cations on the A-site of the perovskite structure. However, the chemical and structural stabilities under operation-relevant conditions are insufficient [9–12]. Starting from the SCF material system, the introduction of barium on the A-site of the perovskite lattice causes an ordering of the oxygen vacancies and prevents the transition to the orthorhombic SCF brownmillerite

structure [13–15]. The partial substitution of strontium by barium was found to increase oxygen permeation flux through the membrane and enhances phase stability of the cubic phase at high temperature [9,14,16,17]. However, the introduction of higher Ba-concentrations (more than 50% of the A-site cations) also increases the Goldschmidt tolerance factor leading to the instability of the perovskite structure and the formation of hexagonal barium oxides [14,18–20]. Nevertheless, the stoichiometry $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) in its cubic perovskite phase was reported to exhibit superior oxygen-flux rates combined with high phase stability even at low oxygen partial pressures [9,21,22]. More recent investigations of the phases in BSCF indicate a phase transition of the cubic perovskite into a hexagonal phase within the temperature range of 800 °C to 900 °C [11,12,23,24]. The pathway of this transition may first lead to a monoclinic phase, which was regarded as intermediate step towards the formation of the hexagonal phase [11]. The reason for the degradation of the cubic perovskite phase could be the reduction of the ionic radius of cobalt caused by a change of the valence state from Co³⁺ to Co²⁺. Efimov et al. recently presented a first detailed investigation of the phase composition of BSCF5582 by transmission electron microscopy (TEM) [24]. They studied samples annealed at 750 °C and 800 °C and observed the formation of a 15R hexagonal polytype with lamellar morphology in addition to the hexagonal phase. The formation of non-cubic phases in perovskites limits the performance of the oxygen ion conductor, as any deviation from the cubic perovskite structure reduces the symmetry of the crystal and increases lattice stress. This leads to a worse mobility of the oxygen vacancies

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[25,26]. For BSCF, a degradation of the oxygen ion conduction due to phase conversions was reported by different groups [9,10,27].

To further elucidate the complex decomposition of the cubic BSCF5582 phase we have carried out a study in a large range of annealing temperatures between 700 °C and 1000 °C. The decomposition kinetics at 800 °C is studied by investigating samples after annealing periods ranging from 10 h to 1350 h. XRD and different electron microscopic techniques are used to analyze the crystal structure and chemical composition of the three different crystalline phases. We present an etching technique which yields, in combination with scanning electron microscopy, estimates of the volume fraction of the different phases. In addition to the well-known cubic and hexagonal phases we focus on the properties of the second phase with non-cubic structure which is observed in the temperature range between 700 °C and 900 °C.

2. Sample fabrication and experimental techniques

The BSCF powder was synthesized by the solid state reaction route, by mixing stoichiometric amounts of commercial BaCO₃, SrCO₃, Co₃O₄ and Fe₂O₃ powders from MERCK (Darmstadt, Germany). The raw powders were first mixed, and then calcined at 950 °C for 10 h and finally ground by ball-milling to a particle size of about 3.1 μm.

Short-time ($t = 10$ h) annealed BSCF5582 compacts ($5 \times 4 \times 10$ mm³) were prepared by isostatic pressing of powder at 200 MPa and subsequent temperature treatment at 700 °C, 800 °C and 900 °C without any pre-sintering at higher temperatures.

BSCF5582 bulk samples ($2 \times 5 \times 5$ mm³) for long-time ($t \gg 10$ h) annealing were fabricated from commercially available BSCF5582 powder with a D_{50} value of 2.4 μm by uniaxial pressing (ca. 100 MPa) and sintering at 1000 °C for 12 h. The samples were subsequently annealed at temperatures of 800 °C and 850 °C for different time periods (100 h–1350 h). The cooling rate after annealing was 20 K/min. A list of the different investigated bulk samples is given in Table 1.

An overview of the crystalline phases in the BSCF5582 samples was obtained by X-ray diffractometry (XRD) which was carried out in a Siemens D-5000 spectrometer (Bruker AXS, Karlsruhe, Germany) with CuK_α radiation and a scintillation detector. All measurements were performed 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_{α2}-radiation, using the program EVA (Bruker AXS).

Detailed microstructure characterization was carried out by different electron microscopic techniques. Scanning electron microscopy (SEM) was performed on polished and chemically etched surfaces with a Zeiss 1530 Gemini scanning electron microscope operated at electron energies between 5 and 15 keV. The sample surfaces were etched with a colloidal silicon dioxide solution (Oxid Polier Suspension, Oberflächentechnologien Dieter Ziesmer, Germany) as a last preparation step, resulting in a distinct surface topography and optimum contrast between different phases. SEM images were usually taken with the in-lens detector. Volume fraction estimates of different phases were obtained by contrast analysis of SEM images. Crystallites with

different contrast could be assigned to the different phases on the basis of chemical analyses using EDXS. To normalize the content of the different phases with respect to a pore-less sample, the volume fraction of pores was estimated by defining contrast thresholds which allow a clear distinction between pores and sample.

TEM and scanning transmission electron microscopy (STEM) investigations were performed using a Zeiss Omega 922, a Philips CM200FEG/ST, and a FEI TITAN³ 80–300 transmission electron microscope, operated at 120, 200 and 300 keV respectively. Crystal structure analysis was performed by selected area electron diffraction (SAED) and convergent-beam electron diffraction (CBED). To reduce the influence of damage by high-energy electrons and to improve contrast, CBED patterns were taken using a cooling holder. Electron diffraction patterns were recorded along different zone axes to determine the symmetry of the crystal structure. Experimental SAED patterns were compared with simulated patterns of different BSCF crystal structures reported in literature [11,12,28,29]. Zone axes and lattice parameters were determined using the JEMS software package [30]. The CBED patterns were evaluated with the method described by Morniroli and Steeds based on the work of Buxton et al. which yields three-dimensional (3D) information on the crystal structure [31,32].

The chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDXS) in the FEI Titan³ 80–300 microscope in STEM mode. Composition quantification of EDXS spectra was performed with the FEI “TEM imaging and analysis” (TIA) software (Version: 3.2 SP6 build 421). Cation concentrations were calculated on the basis of the TIA software using a refined Kramer's law model which includes corrections for detector absorption. The calculations are based on standard-less quantification without thickness and background correction.

TEM sample preparation was carried out by conventional methods, which include grinding, polishing and Ar-ion etching. Additionally, TEM samples of individual crystals within the BSCF bulk samples were fabricated by site-specific preparation in a focused-ion-beam (FIB) system using the technique described by Ayache et al. [33]. This allows the fabrication of TEM lamellae with different distinct zone-axis orientations.

3. Experimental results

The following chapter is subdivided into three subchapters. Section 3.1 outlines the results of the XRD and SEM studies. Section 3.2 focuses on the structural analyses by TEM and Section 3.3 contains the results of chemical analyses by EDXS.

3.1. Scanning electron microscopy and X-ray diffractometry

Fig. 1 shows XRD spectra of a single sample of cubic BSCF powder after calcination (Fig. 1(a)) and annealing in ambient air at 800 °C for 72 h, 120 h, 240 h, 600 h and 1680 h (Fig. 1(b–f)). The cooling and heating rate between the annealing steps was set to 20 K/min. The analysis of the XRD pattern Fig. 1(a) yields only the cubic perovskite structure with a lattice parameter of 3.986 Å, which agrees well with literature data [12,28]. All nine reflections in the 2θ -range from 20° to 80° were fitted using WinINDEX (Bruker AXS) with only one possible result with a figure of merit (FoM) of 363. Upon annealing, the formation of a hexagonal phase can be observed resulting in a mixture of cubic and hexagonal BSCF. The hexagonal reflections – corresponding to the (101), (201) and (112) planes – are already clearly detectable after 72 h and continue to gain in intensity with increasing annealing time. A WinINDEX fit of the Bragg reflections of the hexagonal phase in the 2θ -range from 20° to 80° yields hexagonal lattice constants $a = b = 5.629$ Å and $c = 4.361$ Å (the low-intensity reflection of the hexagonal phase at $2\theta \approx 73^\circ$ was omitted). This is in good agreement with the values determined by e.g. Švarcová et al. [12].

Table 1
Overview of the BSCF5582 bulk samples.

Temperature [°C]	Annealing time [h]	Sample denotation
700	10	BSCF700-10
800	10–1350	BSCF800-xxx
850	200	BSCF850-200
900	10	BSCF900-10
1000	10	BSCF1000-10

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