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Abstract
Perovskite-type membranes of (Ba0.5Sr0.5)(Co0.8Fe0.2)O3−δ (BSCF) and (Ba0.5Sr0.5)(Fe0.8Zn0.2)O3−δ (BSFZ) were successfully prepared via liquid-phase sintering using BN as sintering aid. The obtained membranes were examined via powder X-ray diffraction pattern (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and oxygen permeation experiments. It has emerged that the use of BN as sintering aid lowers sintering temperatures in order to obtain dense membranes with relative densities in the range of 93–96% as proven by the Archimedes method. It was further shown that the perovskite structure could be maintained after sintering with BN. Additionally, BN was completely removed from the sintered membranes. Investigation of the microstructure revealed that the average grain size of the membranes was influenced by the amount of BN added prior the sintering process. It was found that large amounts of BN effectively lower the average grain size. Oxygen permeation experiments have shown that the lower the average grain size the lower the oxygen permeation performance, particularly in the case of BSCF. Transmission electron microscopy revealed that no evidence for an amorphous layer or any other interfacial phase in the grain boundary is present.

Keywords: BSCF; BSFZ; Oxygen permeation; Grain boundaries; Transmission electron microscopy; Perovskite; Liquid-phase sintering; BN; Grain size distribution

1. Introduction
Nowadays, mixed ionic–electronic conductors (MIECs) with perovskite structure are applied in many different processes as they allow to selectively separate oxygen from gaseous mixtures. Due to their intrinsic mixed conductivity, they are of great interest for many industrial processes in which a constant supply or removal of oxygen to or from reaction mixtures is required [1]. Applications such as the usage of MIEC as cathode material in solid-oxide fuel cells as well as in the production of oxygen enriched air and in the conversion of hydrocarbons to synthesis gas have been reported [2–6]. Major advantages of these membranes are their almost infinite permselectivity and remarkable high oxygen fluxes in the range observed on microporous materials [1].

Within the MIECs, (Ba0.5Sr0.5)(Co0.8Fe0.2)O3−δ (BSCF) is regarded to be one of the most promising materials as membranes made of it show high oxygen permeation fluxes and excellent phase stability even under low oxygen partial pressures and reducing gas atmospheres [7–9]. Recently, a new perovskite system (Ba0.5Sr0.5)(Fe0.8Zn0.2)O3−δ (BSFZ) was invented which also exhibits excellent phase stability and remarkably high oxygen fluxes [10–12]. As these perovskite systems display two of the state-of-the-art materials, they are of special interest and thus investigated regarding their microstructure and oxygen permeation performance in the presented study.

Several groups have reported that the microstructure and thus the relation between bulk and grain boundary oxygen ion diffusivity within dense ceramic membranes significantly influences the oxygen permeation performance [13–19]. Different perovskite systems were studied in these reports and no clear trend is visible whether the transport along grain boundaries displays a barrier or acts as a pathway for fast oxygen transport. Diethelm et al. found for (La0.5Sr0.5)FeO3−δ that the larger the obtained grains – and thus the fewer the grain boundaries – the smaller the observed oxygen permeation performance [13–14]. Similar findings were reported for LaCoO3−δ by Kharton and Marques [15]. Contrary to that, in ceramics
of Ca(Ti$_{0.8}$Fe$_{0.2}$)O$_{3-δ}$ – prepared by mechanical activation – grain boundaries are suggested to act as a barrier for oxygen permeation [16]. Most remarkably, opposite results were found within the system (Ba$_{1−x}$Sr$_x$)(Co$_{0.8}$Fe$_{0.2}$)O$_{3-δ}$. The end member Sr(Co$_{0.8}$Fe$_{0.2}$)O$_{3-δ}$ provides improved oxygen permeation performance by decreasing the average grain size, whereas for (Ba$_{0.5}$Sr$_{0.5}$)(Co$_{0.8}$Fe$_{0.2}$)O$_{3-δ}$ opposite observations have been obtained [17–19]. As several parameters during the preparation influence the properties of the membrane, the effect of the microstructure on the oxygen permeation has to be studied more systematically. This could be done by varying the microstructure in different perovskite systems via the same way, i.e. the sintering temperature and dwelling time. Additionally, care has to be taken by comparing results, if the raw perovskite powder has been prepared in different ways, which might also influence the properties of the final membrane.

In this study, we have applied a liquid-phase sintering to obtain BSCF and BSFZ membranes using BN as sintering aid. The method was described by Ho on the BaTiO$_3$ perovskite system [20]. It was shown that the application of BN as sintering aid allows to lowering the sintering temperature, and no incorporation of boron into the perovskite lattice was observed. Due to the fact that during the sintering process a liquid-phase is eminent in the membrane, a lowering of the average grain size is expected [21]. In order to study the changes in microstructure and its influence on the oxygen permeation performance, membranes of BSCF and BSFZ with varying BN content during sintering were prepared. Investigations of the microstructure were carried out by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDXS). Transmission electron microscopy (TEM) along with EDXS and electron energy-loss spectroscopy (EELS) was conducted to examine the microstructure and elemental composition of grain boundaries. Additionally, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and oxygen permeation experiments as well as relative density measurements were applied for characterization purposes.

2. Experimental

BSCF and BSFZ powders were synthesized via a combined citrate and ethylene-diamine-tetraacetic acid (EDTA) complexing method according to Shao et al. [9]. Proper amounts of Ba(NO$_3$)$_2$, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$.6(H$_2$O), Fe(NO$_3$)$_3$.9(H$_2$O), and Zn(NO$_3$)$_2$.2(H$_2$O) were dissolved in water, followed by the addition of citric acid, EDTA and NH$_3$.H$_2$O. The reaction mixtures were then heated under constant stirring to obtain a purple-coloured gel. Afterwards the gels were pre-calcined for 2 h at 700 °C. The pre-calcined powders were ground and finally fired for 10 h at 950 °C to get the pure perovskite phases. The pure perovskite powders were then carefully grounded together with certain amounts of hexagonal-BN (space group: $P6_3/mmc$ (194), $a = 2.5044$ Å, $c = 6.6562$ Å; Powder Diffraction File: 34–421, average particle size of $\Omega = 1 \mu$m): 2.5, 5, 7.5, and 10 mol%. The grounded powders were then coldly pressed under 140–150 kN for 20 min to prepare "green" membranes which were finally sintered at 1050 °C (BSCF) and 1100 °C (BSFZ) with a dwelling time of 10 h in an ambient air atmosphere. In order to estimate the optimal sintering temperature, the melting point of each membrane was measured via (DSC) on a SETSYS TGA-DSC instrument. Relative densities of the sintered membranes were acquired via the Archimedes method on a Sartorius balance model BP 211D with a resolution of 0.01 mg equipped with compatible attachment.

To study the oxygen permeation performance of the sintered membranes, several permeation experiments were carried out on a self-made high temperature permeation cell which is described in detail elsewhere [18]. Discs of BSCF and BSFZ (Ø = 14 mm, thickness = 1.15 mm) were sealed onto a ceramic tube with gold-paste (conducting paste, C5754, Heraeus) at 950 °C for 2 h. After sealing, gas flow rates were delivered to the reactor by mass flow controllers (Bronkhorst Hi-Tech) and continuously read by an on-line gas chromatograph (Agilent Technologies, HP 6890, equipped with a Carboxen 1000 column). The feed side (outer side of the ceramic tube onto the membrane was sealed) pure helium and neon were applied. The total flow rate on the feed side of the membrane was set to be 150 ml/min, and the total flow rate on the sweep side to 30 ml/min. The absolute flow rate of the permeate stream (sweep plus permeated oxygen plus leakage) was determined by using neon as an internal standardization. The permeate stream (consisting of helium, oxygen, nitrogen, and neon) was examined by gas chromatography. For each component a quantitative calibration with known standards was conducted. Thus, the area of each component chromatogram was directly related to a certain percentage of this component. As the supplied sweep flow rate (i.e. helium and neon with no permeated oxygen) was known, it was thus possible to determine the total permeate flow rate from the concentration of neon in the permeate stream. The total leakage (<5%) was calculated by the amount of nitrogen, i.e. the percentage nitrogen found in the permeate stream was treated as the leakage. The related amount of oxygen was then subtracted from the total oxygen in the chromatogram leading to the net permeated oxygen. The permeation flux through the membrane could then be calculated by the fraction O$_2$ in the effluents and the determination of the effective permeation area of the membranes. Permeation experiments were conducted in the temperature range from 800 to 925 °C with steps of 25 °C. For each temperature step, an equilibrium time of 60 min was set. The actual temperature was measured slightly above the membranes.

In order to analyze the microstructure of the sintered membranes, SEM combined with EDXS as well as XRD were conducted on both surfaces and on fracture surfaces. Grain size distributions were evaluated by SEM on a JEOL JSM-6700F field-emission instrument using a secondary electron detector (SE) at an accelerating voltage of 2 kV. Fracture surfaces were etched with aqueous HCl (2 M) for 2–5 s in order to visualize grain boundaries. EDX spectra were obtained at an accelerating voltage of 15 kV using a light-element detector (INCA 300, Oxford Instruments). To determine the crystal structure of sintered membranes, XRD were conducted with monochromated Cu K$_{α1}$ radiation in the range of 20–50° 2θ at room temperature.
Fig. 1. DSC data obtained from a “green” BSCF membrane containing 10 mol% BN in a synthetic air atmosphere. The asterisk indicates a sensitivity switch of the instrument.

(Philips X’Pert-PW1710) on surfaces and grounded membranes. Powder XRD data for interpretation were taken from literature, ZnO: ICDD database PDF number [36–1451], BSCF [22], BSFZ [23].

Additionally, TEM was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. EDXS was carried out by a light-element detector using the Cliff–Lorimer quantification technique (INCA 200 TEM, Oxford Instruments). Furthermore, the specimen for TEM investigations was prepared as follows. First, pieces of 1 mm × 1 mm × 2 mm were cut out of the membrane followed by covering of both sides with silicon single crystal using epoxy. Accordingly, the protected membrane pieces were polished on polymer embedded diamond lapping films down to 0.02 mm × 1 mm × 2 mm and glued onto a copper slot grid. Electron transparency was achieved by Ar+ ion sputtering at 3 kV under incident angles of 6° and 4° (Gatan, model 691 PIPS).

3. Results and discussion

Fig. 1a and b shows DSC data obtained from a “green” BSCF membrane containing 10 mol% BN in a synthetic air atmosphere. Around 800 °C (point 1), BN starts to oxidise yielding in B2O3 as indicated by an endothermic process. As B2O3 starts to melt immediately after oxidation, we postulate that the endothermic process of oxidation covers the endothermic melting process. Thus, the heat flow of this melting process is not directly visible. At 1078 °C (point 2), an endothermic heat flow is observed, which is clearly related to the melting process of the membrane followed by the decomposition of the melt.

For both materials, BSCF and BSFZ, respectively, excellent phase maintenance after sintering with BN has been observed as it can be concluded by comparing the obtained XRD pattern with those obtained from pure BSCF and BSFZ powders [22,23] as visible in Fig. 2a and b. Despite the fact the perovskite structure could be maintained even after sintering with BN, small amounts of CoO have been found in the BSCF membrane that was sintered with 10 mol% (not visible in XRD pattern but confirmed by EDXS of the fracture surface). In the case of BSFZ membranes that were sintered with 7.5 and 10 mol% small amounts of ZnO...
have been detected on the surface as shown in Fig. 2b. Additionally, two unidentified reflections with very low intensities at $28.6^\circ \, 2\theta$ and $30.4^\circ \, 2\theta$ were found in these membranes.

In order to examine the microstructure of the sintered membranes, SEM was conducted on both surfaces and fracture surfaces on each membrane (Figs. 3 and 4). Fig. 3 displays SEM micrographs and corresponding grain size distributions of BSCF membranes after sintering with 2.5 mol\% BN (a–c) and with 10 mol\% BN (d–f) for 10 h at $1050^\circ C$, respectively. As it can be seen in Fig. 3, dense membranes of BSCF sintered with BN have been achieved with low level of porosity even if the sintering temperature was decreased to $1050^\circ C$. Wang et al. found...
that sintering temperatures of at least 1150 °C were needed to obtain dense BSCF membranes with negligible porosity [18]. Obviously, the sintering aid BN helped to lower the sintering temperature of the prepared dense membranes. This was confirmed by DSC, as the melting point of the membranes was decreased using BN as sintering aid. A summary of the melting temperatures of the sintered BSCF and BSFZ membranes is given in Table 1.

Quantitative evaluation of the grain size distribution via SEM have shown that the addition of large amounts of BN lead to a decrease of the average grain size (Fig. 3c and f). The average grain size of BSCF-membranes sintered with 2.5 mol% BN has been determined to be 242 ± 10 μm² at the surface and 265 ± 15 μm² at the fracture surface, respectively. Contrary, membranes sintered with 10 mol% BN exhibit average grain sizes of 140 ± 5 μm² (surface) and 155 ± 15 μm² (fracture surface). In the case of 10 mol% BN, small particles of CoO (∼1 μm²) have been found on the fracture surface as confirmed by EDXS.

Similar experiments were conducted for membranes of BSFZ. It has emerged, that melting temperatures of BSFZ membranes with BN as sintering lie generally up to 70 °C higher than that for the BSCF membranes (Table 1). In Fig. 4, SEM micrographs and grain size distributions of membranes after sintering with 2.5 mol% BN (a–c) and membranes sintered with 10 mol% BN are displayed (d–f). As for the case of BSCF, BSFZ membranes sintered with BN exhibit a low level of porosity and the same trend for the average grain size was found as for the BSCF membranes: The higher the amount of added BN the lower the average grain size. The average grain size of BSCF membranes sintered with 2.5 mol% BN has been determined to be 1131 ± 5 μm² at the surface and 1218 ± 8 μm² (fracture surface) if 10 mol% BN were added (Fig. 4d and f). It has to be noted that small particles of CoO (∼1 μm²) of ZnO (∼1 μm²) were found on the membrane surface in membranes of BSFZ membranes sintered with 10 mol% BN.

Table 2
Summary of average grain sizes in sintered membranes with varying BN content

<table>
<thead>
<tr>
<th>BN (mol%)</th>
<th>BSCF (area μm²) (surface)</th>
<th>BSCF (area μm²) (fracture surface)</th>
<th>BSFZ (area μm²) (surface)</th>
<th>BSFZ (area μm²) (fracture surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>242</td>
<td>265</td>
<td>2.5</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
<td>218</td>
<td>5</td>
<td>68</td>
</tr>
<tr>
<td>7.5</td>
<td>216</td>
<td>199</td>
<td>7.5</td>
<td>46</td>
</tr>
<tr>
<td>10</td>
<td>140</td>
<td>155</td>
<td>10</td>
<td>38</td>
</tr>
</tbody>
</table>

Sintering with 2.5 mol% BN (a–c) and membranes sintered with 10 mol% BN are displayed (d–f). As for the case of BSCF, the higher the amount of added BN as in the case of BSFZ membranes sintered with BN, the oxygen permeation is observed in the temperature regime studied here. BSCF membranes sintered with 2.5 mol% BN exhibit an oxygen permeation performance that varies from 1.50 ml/min cm² at 850 °C to 2.60 ml/min cm² at 925 °C. As the amount of BN was increased during sintering, a diminution of the oxygen permeation flux has been observed (0.80 ml/min cm² at 850 °C to 1.60 ml/min cm² at 925 °C for 10 mol% BN added). In the case of BSFZ membranes sintered with BN, the oxygen permeation performance is not as strongly affected by the addition of BN as in the case of BSCF. Up to 7.5 mol% BN added as sintering aid no change in the oxygen permeation performance could be found and its ranges from 0.40 ml/min cm² (850 °C) to 0.85 ml/min cm² (925 °C) which is in the same order of magnitude as reported for membranes without sintering aid [10]. Only if the BN addition was set to 10 mol%, a distinct diminution in the oxygen permeation performance has been observed, as the oxygen permeation flux is found to range between 0.37 ml/min cm² (850 °C) and 0.80 ml/min cm² (925 °C) in this case.

In order to better visualize the dependence of oxygen permeation performance on the amount BN added to the membranes...
before sintering, oxygen permeation fluxes are plotted against the BN content and the average grain size on the surface at fixed temperature (Fig. 6a and b). At a temperature of 900 °C the oxygen permeation decreases from 2.30 ml/min cm² (2.5 mol% BN) down to 1.40 ml/min cm² (10 mol% BN) for BSCF membranes, whereas the oxygen permeation flux of BSFZ membranes range from 0.80 down to 0.70 ml/min cm² at 900 °C (Fig. 6a). The influence of the average grain size of the membranes on the oxygen permeation performance is displayed in Fig. 6b. For the case of BSCF membranes a decrease of the oxygen permeation flux from 2.30 down to 1.40 ml/min cm² is observed whereas the corresponding average grain size ranges from 265 to 155 μm² at the fracture surface. It should be stressed that the oxygen permeation performance decreases proportionally to the average grain size. In order to draw a general conclusion, membranes that have been sintered without boron nitride were also studied. Permeation experiments show that membranes consisting of an average grain size of 468 μm² (surface) and 430 μm² (fracture surface) exhibit an oxygen flux of 2.70 ml/min cm² at 900 °C, which is in excellent agreement with results discussed above.

In the case of BSFZ, the oxygen permeation flux varies from 0.77 to 0.72 ml/min cm² at 900 °C whereas the average grain size at the fracture surface ranges from 93 to 24 μm².

Again, membranes without BN addition were prepared. It was found that a membrane with an average grain size of 435 μm² (surface) and 317 μm² (fracture surface) show an oxygen permeation flux of 0.80 ml/min cm² at 900 °C, which is higher than in the case of the membrane sintered with 2.5 mol% BN (oxygen permeation flux for this membrane: 0.77 ml/min cm²).

In the case of BSCF, it is obvious that the larger the grain sizes the greater the oxygen permeation flux. This is in good agreement with findings of Wang et al. who also found a positive correlation between larger grains and higher oxygen permeation flux[18]. BSFZ membranes do not exhibit an influence of the average grain size that is as strong as for BSCF membranes.

In order to achieve a better understanding of the microstructure at the grain boundaries, an HRTEM study was conducted on a BSCF membrane which was sintered with 10 mol% BN as it is shown in Fig. 7. A TEM micrograph of two BSCF grains which can be discriminated by bright contrast is displayed in Fig. 7a. BSCF stoichiometry of these two grains has been confirmed by an EDXS analysis. For that purpose an ovaly shaped convergent electron beam was used. The convergent beam mode allows to acquire as much signal as possible from the grain boundary.
From the EDXS analysis no difference in the elemental composition of grain I, grain II, and the grain boundary have been found as it can be seen in Table 4. As EDXS might not be the most sophisticated method to elucidate light elements like boron, electron-energy loss spectroscopy (EELS) was also conducted. Even via EELS, no boron could be found. Fig. 7b and c show HRTEM micrographs of a selected part of this grain boundary. Neither an interfacial phase nor an amorphous layer has been found to be located between the two grains as it can be seen in Fig. 7c. No zone axis could be determined for grain I but the observed plane spacing was determined to be 0.23 nm which is related to the (1,1,1)-plane of BSCF. The zone axis of grain II was found to be [1,1,1]. Thus, the grain boundary displays the contact zone between (1,1,1)-planes of grain I and (1,1,0)-planes of grain II whereas the angle between these planes is determined to be 21°. An inverse fast-Fourier transformation (based on (1,1,1) of grain I and (1,1,0) of grain II) was conducted which is shown in Fig. 7d. As indicated by black lines, Moiré pattern has been observed indicating an overlap of approximately 6 nm of grain I and grain II. As the contrast of the lattice planes do not abate towards the contact zone, no indication for an amorphous layer is given. Diethelm et al. suggested that in the case of (La0.5Sr0.5)FeO3−δ an amorphous layer at the most of 0.5 nm may be prominent [13,14]. As reported for this material, smaller average grain sizes promote the oxygen permeation flux. Thus, the amorphous layer may act as fast diffusion pathway. This finding could further deliver an explanation for the blocking effect of the grain boundaries in the study presented here, as we believe no amorphous or interfacial layer is eminent in the grain boundaries of BSCF. Feldhoff et al. [11] reported even in BSFZ the grain boundaries are atomically thin containing no second phase, which underlines the findings presented here.

Table 4
Quantitative analysis of elemental composition by EDXS of grain I, grain II and grain boundary as shown in Fig. 7

<table>
<thead>
<tr>
<th>Element</th>
<th>Grain I (atom%)</th>
<th>Grain II (atom%)</th>
<th>Grain boundary (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>28</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>Sr</td>
<td>24</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>Co</td>
<td>37</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>Fe</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
</tbody>
</table>
4. Conclusion

Dense ceramic membranes of BSCF and BSFZ with BN as sintering aid were successfully prepared via liquid-phase sintering. It has emerged that using BN as sintering aid the sintering temperature could be lowered down to 1050 °C in the case of BSCF membranes and down to 1100 °C in the case of the BSFZ membranes. It is also shown that the obtained membranes exhibit excellent phase stability after sintering with only very few impurities and no boron remained in the membranes after the sinter process. For both membrane materials BSCF and BSFZ, an increase of the added amount BN lead to a decrease of the average grain size. Oxygen permeation experiments delivered evidence that membranes containing particularly larger grains exhibit a better oxygen permeation performance. This effect is especially pronounced in the case of BSCF membranes in which the oxygen permeation flux is lowered proportionally to the abatement of the average grain size. A TEM study gives first indication that no amorphous material or interfacial phase is incorporated at the grain boundaries. That leads to the assumption that a lattice misfit between the grains and associated straining of grain boundary near regions could have negative impact on the oxygen ion transport. Considering former reports on the correlation of microstructure and oxygen permeation, future investigations should focus on the microstructure of the grain boundaries as their nature may give a better understanding of the oxygen permeation through dense ceramic membranes.

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