Densification and Proton Conductivity of La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ Electrolyte Membranes

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Abstract: Bain La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ impairs sintering and leads to a decrease in its ceramic density. Two approaches have been studied for obtaining dense ceramics: using a high processing temperature and the introduction of a Co$_2$O$_3$ sintering additive. An addition of only 0.5 wt% of Co$_2$O$_3$ sintering additive, despite the positive sintering effect, causes a noticeable violation of stoichiometry, with partial decomposition of the material. This can lead to the formation of cationic vacancies, which form associates with oxygen vacancies and significantly reduce the oxygen ion and proton conductivity of the materials. There is also a partial substitution of Co for Sc in La$_{1-x}$Ba$_x$ScO$_{3-\delta}$, which reduces the stability of protons: it reduces the enthalpy of the hydration reaction, but increases the mobility of protons. Thus, the Co$_2$O$_3$ sintering additive causes a complex of negative effects on the conductivity of La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ materials. Only high-temperature (1800 °C) processing with protection against Ba loss contributes to the production of dense La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ ceramics. The chemical composition of such ceramics corresponds well to the specified one, which ensures high water uptake and, consequently, high proton conductivity.

Keywords: proton conductivity; lanthanum scandate; sintering additive

1. Introduction

Materials with proton conductivity are currently one of the most interesting among solid oxide materials. Among proton-conducting oxides, the highest proton conductivity is realized in acceptor-doped materials with a perovskite-type structure, which makes them promising for use in electrochemical devices, for example, as solid electrolytes for proton–ceramic fuel cells, gas sensors, etc. [1–8]. Their feature is that proton charge carriers are formed by incorporating water vapor into oxygen vacancies, formed, for example, by introducing a cationic acceptor dopant with a reduced valence:

$$\text{BaO}(-\text{LaO}_1) \rightarrow \text{Ba}_{\text{La}}^+ + \frac{1}{2} \text{V}_{\text{O}}^* + \text{O}_\text{O}^-, \quad (1)$$

$$\text{H}_2\text{O} + \text{V}_{\text{O}}^* + \text{O}_\text{O}^+ = 2\text{OH}^., \quad (2)$$

where $\text{Ba}_{\text{La}}^+$ are Ba dopant atoms in La regular lattice positions, $\text{O}_\text{O}^-$ are oxygen atoms in regular lattice positions, $\text{V}_{\text{O}}^*$ are oxygen vacancies, and $\text{OH}^.$ are proton defects. The perovskite group of the A$^{3+}$B$^{3+}$O$_3$ type, such as La$_{1-x}$M$_x$BO$_{3-\delta}$ (where M = Ca, Sr, Ba; B = Y, Yb, Sc, In) [8–27], are promising ceramic proton conductors because they have
a significant advantage over the widely studied materials based on Ba(Zr,Ce)O$_3$ due to the tendency of Ba to carbonize [28–30]. Systematic studies of the transport properties of La$_{1-x}$M$_x$BO$_{3-\delta}$ demonstrate a tendency for an increase in proton conductivity with an increase in the ionic radius of the dopant and a decrease in the ionic radius of the B-cation [8–27]; thus, the highest proton conductivity should be realized in La$_{1-x}$Ba$_x$ScO$_{3-\delta}$.

Unfortunately, there is no information on La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ ceramic sintering in the literature. Lee et al. [15] do not provide information on the density of La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ ($x = 0.05$–$0.50$) ceramics sintered at 1600 °C (10 h), despite the fact that the crystal structure and conductivity of these materials have been studied in detail in a wide range of Ba concentrations. They showed a change in the crystal structure when the concentration of Ba increases, namely: at $0 \leq x < 0.1$, an orthorhombic structure is formed, at $0.1 \leq x < 0.3$, a mixture of orthorhombic and cubic is formed, and at $0.3 \leq x \leq 0.5$, only a cubic structure is presented. Kendrick et al. [31] carried out multiple anneals at 1500 °C (10 h) to prepare single-phase La$_{0.5}$Ba$_{0.4}$ScO$_{3-\delta}$, but obtained an actual Ba content of 0.27 and an orthorhombic structure, as well as an impurity of Sc$_2$O$_3$, which is detectable only due to the neutron diffraction technique.

On the example of La$_{1-x}$Ba$_x$ScO$_{3-\delta}$, it was shown that even the use of a small amount of Ba can complicate the sintering of ceramics. Kasyanova et al. [26] showed that the sintering of La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ ($x = 0.03$–$0.1$) ceramics significantly deteriorates at 1400 °C (5 h) at a concentration of Ba $x \geq 0.05$. On the other hand, Obukuro et al. [27] demonstrated the production of high-density ceramics (more than 95%) of La$_{1-x}$Ba$_x$YbO$_{3-\delta}$ ($x = 0.02$–$0.1$) after multistage synthesis and long-term sintering (10 h) at 1700 °C, although the authors did not check the Ba losses.

An alternative way to improve the sinterability of ceramics can be the introduction of small amounts of sintering additives, most often, transition metal oxides, into the pre-synthesized powder [32,33]. However, the sintering additive can negatively affect the water uptake and ionic conductivity of Ba-doped LaScO$_3$, as shown in recent studies for Ba(Zr,Ce,Y)O$_3$ materials [34–37]. The incorporation of over-stoichiometric transition metal atoms into the crystal lattice of proton-conducting materials generally has a negative effect on hydration, in particular, by reducing the saturation limit of protons. According to a study by Han et al. [33], oxides of Co and Ni in the Mn-Fe-Co-Ni series have the least negative effect on the proton transport of Ba(Zr,Y)O$_3$ materials. We have previously identified Co$_3$O$_4$ among transition metal oxides as the optimal sintering additive for La$_{0.9}$Sr$_{0.1}$ScO$_{3-\delta}$ [8], while the effect of the same additive on La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ has not been studied.

In this research, we investigated the effect of heat treatment regimes, as well as 0.5 wt% Co$_3$O$_4$, on the sintering process and microstructure, crystal structure, water uptake, and proton conductivity of the La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ proton-conducting materials.

2. Materials and Methods

Materials of composition La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ (where $x = 0.025$, 0.05, 0.075, and 0.1) were synthesized using the citrate–nitrate combustion method. Oxides La$_2$O$_3$ and Sc$_2$O$_3$, and carbonate BaCO$_3$ (all of high pure grade), were used as precursors. Stoichiometric amounts of precursors, taking into account their weight loss coefficients during calcination, were converted to a nitrate solution using a nitric acid. After complete dissolution of all precursors, citric acid was added to the resulting mixture and evaporated until the combustion reaction proceeded. The powders obtained after drying were annealed at a temperature of 800 °C for 2 h for decarbonization, after which the powder mixture was homogenized in isopropyl alcohol using a PM 100 zirconia-based planetary ball mill (Retch GmbH, Haan, Germany) for 1 h (350 rpm). Dried powders of all compositions were subjected to preliminary synthesis at 1200 °C for 2 h. Parallel to the above path, 0.5 wt% Co$_3$O$_4$ (high pure grade) was added above the basic stoichiometry to the La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ powder obtained after annealing at 800 °C, after which this mixture was homogenized in the planetary ball mill for 1 h (350 rpm) and calcined in air at 1200 °C for 2 h.
From the powders obtained by two above methods, compacts were made using a uniaxial hydraulic press at 400 Pa, which were then covered in the sacrificial powder of the same composition and sintered in air at 1650 °C for 5 h. In the case of sample La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ obtained after two preliminary sintering at 1400 °C (1 h) and 1650 °C (5 h), additional sintering was carried out in a vacuum furnace at 1800 °C for 2 h using a sacrificial powder of the appropriate composition. Then, the obtained ceramic samples were calcined in air at 1100 °C for 5 h for oxygen stoichiometry relaxation. The shrinkage of compacts during heat treatment in air was studied by optical dilatometry using an ODP-868 platform (TA Instruments, New Castle, DE, USA) in the temperature range from room temperature to 1575 °C.

The identification of phases, as well as the crystal structure, was carried out using powder X-ray diffraction (XRD) analysis on a D/MAX-2200 diffractometer (Rigaku, Tokyo, Japan). High-temperature XRD analysis was performed in dry air on a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with a XRK-900 high-temperature chamber (Anton Paar, Graz, Austria). In both cases, the Cu Kα radiation was used. A dry atmosphere ($p$H$_2$O = 0.1 kPa) was achieved by gas circulation through a column with zeolites. The measurements were carried out in a temperature range from room temperature to 900 °C, in the heating mode with a step of 20 °C and in the cooling mode with a step of 30 °C and with an exposure time of 8 min at each point. Phase analysis was performed using the DIFFRACplus-EVA software (Bruker, Karlsruhe, Germany) [38] and PDF4 + ICDD database (Release 2021) [39]. The unit cell parameters were calculated using the Celref software (ENSP, Grenoble, France) [40]. Rietveld structure refinement was performed using the DIFFRACplus: TOPAS software (Bruker, Karlsruhe, Germany) [41].

The cross-sections and surface of the ceramic samples were investigated by scanning electron microscopy (SEM) using MIRA 3 LMU equipment (Tescan, Brno, Czech Republic). The elemental distribution was studied by energy-dispersive X-ray (EDX) spectroscopy using INCA Energy 350 X-Max 80 equipment (Oxford Instruments, Concord, MA, USA).

X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a X-ray photoelectron spectrometer equipped with a hemispherical analyzer PHOIBOS-150-MCD-9 and XR-50 source of X-ray radiation (SPECS Surface Nano Analysis GmbH, Berlin, Germany). The spectra were recorded using nonmonochromatized Al Kα radiation (1486.6 eV). The charge correction was performed by setting the Sc 2p peak at 402.0 eV. The background was subtracted by the Shirley method. Quantitative analysis was performed using the integrated intensities of core-level spectra with the cross-sections according to Scofield [42]. The curve fitting was completed with CasaXPS software (Casa Software Ltd., Teignmouth, UK) [43]. The shape of the peaks is approximated by a symmetric function obtained by multiplying the Gauss and Lorentz functions.

The thermal expansion of the dense ceramic bars was studied using a quartz dilatometer and Tesatronic TT-80 equipment (TESA, Renens, Switzerland) from room temperature to 900 °C with a heating/cooling rate of 2 °C min$^{-1}$ in dry air ($p$H$_2$O = 0.1 kPa).

The thermogravimetric analysis (TGA) was performed on the powder samples with a specific surface area of 1.1 ± 0.2 m$^2$/g using a STA Jupiter 449 F3 analyzer (Netzsch, Selb, Germany) with an aSTEAM DV2MK (aDROP Feuchtemeßtechnik GmbH, Fürth, Germany) water vapor generator. The as-prepared powders were heated up to 950 °C and held at this temperature for 8 h under the dry argon. Afterwards, the carrier gas was saturated with water vapor ($p$H$_2$O = 24.3 kPa), and then the increase in weight was recorded upon cooling from 950 °C to 300 °C with a cooling rate of 30 °C h$^{-1}$ and exposure every 100 °C over 2 h. The proton concentration was obtained from the weight change during TGA as follows:

$$\Delta n_{OH} = \frac{2 \cdot \Delta m \cdot M_s}{m_s \cdot M_{H_2O}},$$

where $M_s$ and $M_{H_2O}$ are molecular weights of the oxides and water, and $\Delta m$ and $m_s$ are the weight change and weight of the specimen, respectively.
The total conductivity was measured as a function of the temperature \(T = 900–400\, ^\circ\text{C}\), oxygen partial pressure \(p_{\text{O}_2} = 21.3\, \text{kPa}–10^{-15}\, \text{Pa}\), and water partial pressure \(p_{\text{H}_2\text{O}} = 0.1\) and 2.8 kPa) by the four-probe DC method using an ADAM-3000 instrument (Advantech, Taiwan). The samples were rectangular bars with four Pt electrodes, which were made of dispersed Pt powder and sintered at 1100 \(^\circ\text{C}\) during 1 h. The \(p_{\text{O}_2}\) was controlled by an electrochemical oxygen pump and a sensor based on a yttria-stabilized zirconia (YSZ). The partial conductivities of protons, oxygen ions, and holes were calculated on the basis of the dependences of the total conductivity on \(p_{\text{O}_2}\) and \(p_{\text{H}_2\text{O}}\) in the framework of the approach developed by Frade [44] and Baek [45]. A detailed description of the calculations is given in [24]. The experimental dependences of total conductivity on \((p_{\text{O}_2})^{1/4}\), which were obtained at two humidity values 2.8 kPa and 0.1 kPa, were used for the calculations and are given in the Supplementary Materials (Figure S1).

The electrochemical impedance spectroscopy (EIS) was performed at 450–300 \(^\circ\text{C}\) in wet air using a SP-200 m (Bio-Logic, Seyssinet-Pariset, France). The measurements were carried out in a frequency range of 7 MHz–500 mHz and at a sinus signal amplitude of 100 mV. The impedance spectra were interpreted into bulk and grain boundary (GB) components using an equivalent circuit scheme of \(R_0-(R_1Q_1)-(R_2Q_2)\), where \(R\) is the resistance, \(Q\) is the constant phase element, and the indexes of 1 and 2 correspond to the bulk and GB processes, respectively. \(R_0\) was purposefully introduced in the equivalent circuit scheme; it imitates the origin of the coordinates, providing a correct fitting. In the approximation of equality of the dielectric constants of the bulk and GBs [46], the GB resistance can be converted to a specific value using the formula:

\[
\sigma_{gb}^* = \frac{1}{R_{gb}} \cdot \frac{1}{S} \cdot \frac{C_{bulk}}{C_{gb}},
\]

where \(R_{gb}\) is the GB resistance, \(\frac{1}{S}\) is the geometric parameter, and \(C_{bulk}\) and \(C_{gb}\) are the capacities of the bulk and GB, respectively.

### 3. Results

#### 3.1. Materials Characterization

Figure 1 demonstrates the XRD patterns of prepared and dried powders of \(\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}\) (0–0.1) obtained by combustion synthesis with final calcination at 1650 \(^\circ\text{C}\). The crystal structure of \(\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}\) was characterized as an orthorhombic perovskite with the \(Pnma\) space group. No impurity phases were observed, which corresponds to a wide range of Ba dissolution in \(\text{LaScO}_3\) [15]. An increase in the Ba concentration leads to the gradual displacement of Bragg peaks; thus, the unit cell volume of \(\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}\) increases (Figure 2). This is in a good agreement with the conventional representation of ionic radii by Shannon [47] because the ionic radius of Ba \((r_{\text{Ba}^{2+}} = 1.61\, \text{Å})\) is larger than La \((r_{\text{La}^{3+}} = 1.36\, \text{Å})\). Thus, when Ba replaces La, the crystal lattice of \(\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}\) undergoes expansion [48] according to the equations:

\[
V = 4 \cdot a_p^3,
\]

\[
a_p = \frac{A}{\sqrt{2}} \left( ((1-x) \cdot r_{\text{La}} + x \cdot r_{\text{Ba}}) + r_{\text{O}} \right) + B \left( r_{\text{Sc}} + r_{\text{O}} \right) + C,
\]

where \(a_p\) is the pseudocubic unit cell parameter; \(A, B,\) and \(C\) are empirical parameters equal to 0.816, 1.437, and \(-0.63095\), respectively [48]; and \(r_{\text{La}}, r_{\text{Ba}}, r_{\text{Sc}}, r_{\text{O}}\) are Shannon ionic radii of \(\text{La}^{3+},\, \text{Ba}^{2+},\, \text{Sc}^{3+},\) and \(\text{O}^{2-}\) [47], respectively. In Figure 2 we can see that the theoretically calculated values of the unit cell volume are in good agreement with the values experimentally determined by XRD. It is important to note that we deliberately dried the samples prior to the XRD analysis in order to prevent additional hydration-related materials expansion.
According to Figure 3, the relative density of sintered La$_{1-x}$Ba$_x$ScO$_{3-δ}$ ceramic materials decreases from ~94% for $x = 0.025$ to ~76% for $x = 0.1$. The average grain size also decreases with increases in the Ba concentration. Both trends show the deterioration of the sintering of ceramics based on LaScO$_3$ caused by the presence of Ba, although similar trends were not previously observed for Ca- and Sr-doped LaScO$_3$ [20,21,24]. Thus, obtaining dense La$_{1-x}$Ba$_x$ScO$_{3-δ}$ ceramic materials is a difficult task, and therefore, taking La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ as an example, we considered various strategies for producing dense ceramics.
3.2. Dense Ceramic Formation Strategies

The general scheme for studying the sintering process of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ samples is shown in Figure 4. As you can see in Figure 5, the most intense stage of shrinkage of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ occurs up to a temperature of 1420 °C and is only 6% of the initial compact volume. With a further increase in temperature, the shrinkage rate decreases, since the process of grain growth begins to compete with the shrinkage of the material, which leads to the formation of porous ceramics with a relative density of 82% after sintering at 1650 °C over 5 h (Figure 4a).

Figure 4. Sintering scheme for La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ ceramics. $\rho$ is the relative density, and $S_{av}$ is the average grain size. The explanation for subfigures are in the text of the paper.

Figure 5. Shrinkage of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ and La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ samples during sintering according to optical dilatometry analysis.

Based on the temperature dependence of shrinkage for La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ samples (Figure 5), the pre-sintering temperature was increased from 1200 to 1400 °C, which led to
an increase in the average grain size of the ceramic to $1.72 \pm 0.42 \mu m$, while the relative density still does not exceed 85% after 1650 °C sintering over 5 h (Figure 4b). This result prompted us to carry out additional sintering in a vacuum furnace, where the temperature reached 1800 °C after 2 h. As can be seen from Figure 4c, after vacuum sintering, it was possible to obtain ceramics with a relative density of 98% and an impressive average grain size of 7.08 ± 1.19 µm.

We introduced 0.5 wt% Co$_3$O$_4$ into the synthesized La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ powder, since it was shown earlier [8] that cobalt oxide is the optimal additive for La$_{0.95}$Sr$_{0.05}$ScO$_{3-\delta}$. As Figure 5 shows, the densification process becomes more active with the addition of Co$_3$O$_4$: it begins at 1150 °C and reaches 12% at 1510 °C, and with a further increase in temperature, the sintering rate increases. In this case, the process of grain splicing dominates, which leads to an increase in the density of ceramics up to ~93% after sintering at 1650 °C over 5 h (Figure 4d).

### 3.3. Dense Ceramics Characterization

Figure 6 shows the XRD patterns of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ crushed ceramics: after standard sintering at 1650 °C, vacuum sintering at 1800 °C and sintering at 1650 °C with 0.5 wt% Co$_3$O$_4$ sintering additive at 1650 °C. The perovskite-like structure was confirmed in all cases, and as Table 1 shows, the unit cell parameters for all samples are very similar. In the case of the La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ sample, there are additional XRD peaks that may correspond to Ba$_2$Sc$_2$O$_5$ [49] and peroxide BaO$_2$ impurities.

![Figure 6. XRD patterns of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ samples obtained after standard sintering (1650 °C), vacuum sintering (1800 °C), and sintering with 0.5 wt% Co$_3$O$_4$ additive (1650 °C).](image)

| Sample                              | A, Å  | B, Å  | C, Å  | Volume, Å³ |
|-------------------------------------|-------|-------|-------|------------|
| La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ standard sintering | 5.780 | 8.110 | 5.697 | 267.1      |
| La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ vacuum 1800 °C | 5.784 | 8.105 | 5.692 | 266.9      |
| La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ | 5.778 | 8.106 | 5.693 | 266.7      |

SEM images of cross-sections in Figure 7 demonstrate the absence of closed image pores in the volume of the ceramics. The results of EDX analysis show a homogeneous distribution of La, Ba, and Sc in the vacuum sintered sample (Figure 7a). At the same time, for La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$, a small number of regions with an increased Sc concentration are noted (Figure 7b), which may correspond to Sc$_2$O$_3$. We do not detect areas enriched in Ba, indicating a uniform distribution of Ba in terms of EDX beam size. As
seen from Table 2, the quantitative ratio of cations is in good agreement with the nominal compositions of the samples, although a slight deficit in the sum of La and Ba relative to Sc is observed. In this case, the amount of Ba relative to La is in good agreement with the given one and is equal to 0.05; therefore, in this case, the evaporation of Ba during synthesis does not occur even after high-temperature annealing in a vacuum at 1800 °C. Most likely, the use of sacrificial powder led to this good result.

![Figure 7](image_url)

**Figure 7.** SEM images (BSE mode) of cross-sections for La$_{0.95}$Ba$_{0.05}$ScO$_3$-$\delta$ after vacuum sintering (a) and La$_{0.95}$Ba$_{0.05}$ScO$_3$-$\delta$ + 0.5 wt% Co$_3$O$_4$ (b) with EDX maps of cation distribution.

**Table 2.** Element contents (at. % ± 0.05) in the ceramics cross-sections according to EDX analysis.

| Sample | La | Ba | Sc | Co | [$\text{Ba}/\text{La}$] |
|--------|----|----|----|----|------------------------|
| La$_{0.95}$Ba$_{0.05}$ScO$_3$-$\delta$ vacuum 1800 °C | 47.25 | 2.42 | 50.33 | - | 0.05 |
| La$_{0.95}$Ba$_{0.05}$ScO$_3$-$\delta$ + 0.5 wt% Co$_3$O$_4$ | 46.87 | 2.27 | 49.98 | 0.88 | 0.048 |

Figure 8 shows the Ba3d and Co2p core-level spectra of the La$_{0.95}$Ba$_{0.05}$ScO$_3$-$\delta$ + 0.5 wt% Co$_3$O$_4$ sample. The Ba3d spectra split into the Ba3d$_{5/2}$ and Ba3d$_{3/2}$ components (the spin-orbital splitting is 15.3 eV) due to the spin–orbit interaction. The Ba3d$_{5/2}$ binding energy is 780.0 eV, which corresponds to the Ba$^{2+}$ state [50,51]. The Ba3d and Co2p spectra overlap substantially. For comparison, we present the data for the La$_{0.9}$Sr$_{0.1}$ScO$_3$-$\delta$ + 0.5 wt.% Co$_3$O$_4$ sample, which was studied in detail elsewhere [8]. The Co2p spectra are the Co2p$_{3/2}$-Co2p$_{1/2}$ doublet. Cobalt in the Co$^{2+}$ state is characterized by the Co2p$_{3/2}$ binding energies in the range 780.0–782.0 eV, as well as the presence of an intense (up to 20% of the main peak) ‘shake-up’ satellite in the 786–787 eV region [52–54]. As seen in Figure 8, the Co2p$_{3/2}$ is a symmetric peak at 781.0 eV; thus, the Co2p spectrum for La$_{0.9}$Sr$_{0.1}$ScO$_3$-$\delta$ + 0.5 wt% Co$_3$O$_4$ contains only one Co$^{2+}$ component with a small intensity. This indicates that Co atoms diffused into the bulk of the grains. We expect a similar behavior for the La$_{0.95}$Ba$_{0.05}$ScO$_3$-$\delta$ + 0.5 wt% Co$_3$O$_4$ sample, which allows for a good fitting of the XPS spectrum as a sum of two components: Ba$^{2+}$ and Co$^{2+}$ (Figure 8). Elemental analysis indicates a threefold excess of Ba ([Ba]/[La] = 0.16) and slight excess of La ([La]/[Sc] = 1.2) on the surface of the sample.
Figure 8. Ba3d (blue line) and Co2p (red line) core-levels spectra of La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 and La0.9Sr0.1ScO3-δ + 0.5 wt% Co3O4 samples.

3.4. Thermal Expansion

As shown in Figure 9, the linear dependence of thermal expansion in a dry air atmosphere according to dilatometry and HT-XRD data indicates the absence of structural transitions. Kim et al. [15] mentioned the formation of a mixture of orthorhombic and cubic phases for La1-xBaxScO3-δ with x ≥ 0.1, while Kendrick et al. [31] definitely indicated an orthorhombic structure for La0.73Ba0.27ScO3-δ. For La0.95Ba0.05ScO3-δ, the orthorhombic structure with the Pnma space group is retained up to 900 °C. Dilatometric results show linear expansion of both La0.95Ba0.05ScO3-δ and La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 ceramic samples with thermal expansion coefficient (TEC) values corresponding to 8.9 × 10⁻⁶ K⁻¹, which is close to the values for Ca- and Sr-doped LaScO3 [20,21].

Figure 9. Thermal expansion of La0.95Ba0.05ScO3-δ and La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 ceramic samples in dry air according to dilatometry and HT-XRD.
3.5. Water Uptake

According to Equations (1) and (2), the value of maximal water uptake \( x_{\text{eff}} \) (saturation limit) has to be equal to the Ba acceptor dopant concentration \( n_{\text{OH}} = 0.05 \) for the investigated La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) sample. Figure 10 demonstrates the temperature dependence of the proton concentration in La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) and La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) + 0.5 wt% Co\(_3\)O\(_4\) crushed ceramic samples, which were obtained by TGA. In the case of La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\), the proton uptake saturation limit \( x_{\text{eff}} \) closely approaches the nominal Ba concentration. The calculated thermodynamic parameters of hydration \( \Delta H_{\text{hydr}} \) (standard enthalpy) and \( \Delta S_{\text{hydr}} \) (standard entropy) for La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) were \(-85 \pm 6\) kJ mol\(^{-1}\) and \(-106 \pm 6\) J mol\(^{-1}\) K\(^{-1}\), respectively. These values are more positive than the values of \( \Delta H_{\text{hydr}} \) and \( \Delta S_{\text{hydr}} \) for Ca-doped \([21]\) and Sr-doped \([19,23]\) LaScO\(_3\) at the same concentration of the acceptor dopant. It is found that the proton concentrations for the La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) + 0.5 wt% Co\(_3\)O\(_4\) sample were significantly below the nominal acceptor concentration. Both \( \Delta H_{\text{hydr}} = -62 \pm 2\) kJ mol\(^{-1}\) and \( \Delta S_{\text{hydr}} = -89 \pm 2\) J mol\(^{-1}\) K\(^{-1}\) thermodynamic parameters became even more positive for La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) + 0.5 wt% Co\(_3\)O\(_4\). Thus, the results clearly indicate a negative effect of Co\(_3\)O\(_4\) additive on water uptake, both on the concentration of protons and on the hydration thermodynamics.

![Figure 10](image-url)

Figure 10. Proton concentrations in La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) and La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) + 0.5 wt% Co\(_3\)O\(_4\) samples.

3.6. Conductivity

3.6.1. Total Conductivity

Figure 11 shows the temperature dependencies of the total conductivity of the La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) and La\(_{0.95}\)Ba\(_{0.05}\)ScO\(_{3-\delta}\) + 0.5 wt% Co\(_3\)O\(_4\) samples in oxidizing and reducing atmospheres at \( p\text{H}_2\text{O} = 2.8\) kPa, measured using the 4-probe DC method. The dependencies in a reducing atmosphere demonstrate a clear inflection caused by the superposition of two types of ion transport: proton and oxygen ion. In an oxidizing atmosphere, they have an almost linear form, which is the result of the three charge carriers’ contribution (protons, oxygen ions, and holes). Holes are formed according to the oxidation reaction:

\[
\frac{1}{2} \text{O}_2 + \text{V}^{\bullet\bullet}_O = \text{O}^\iota_O + 2\text{h}^\bullet
\] (7)
where proton and oxygen ion conductivity. The proton mobility was calculated using the formula:

$$\sigma = \frac{\mu H}{e n H}$$

where \( H \) is the proton conductivity, \( n H \) is the proton concentration, and \( e \) is the elementary charge. As Figure 12b shows, with the introduction of the Co3O4 additive, the proton mobility increases. The activation energy (Ea) of the proton mobility is very close, 0.67 eV and 0.68 eV for La0.95Ba0.05ScO3-δ and La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4, respectively.

3.6.3. Bulk and GB Conductivity

The conductivity of the bulk and grain boundaries (GB) of the La0.95Ba0.05ScO3-δ and La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 ceramics was measured in the temperature range 300–450 °C in a humidified oxidizing atmosphere using EIS. Figure 13a shows the typical impedance spectra of the samples studied, and Figure 13b shows the corresponding equivalent circuits. Figure 13c shows the temperature dependences of bulk and GB conductivity, and in Figure 13d, they are shown as \( \sigma_{GB}/\sigma_{Bulk} \) ratios. The difference between the GB and bulk conductivities of La0.95Ba0.05ScO3-δ increases with decreased in temperature, resulting in the significant impact of the GB contribution. The bulk conductivity of the La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 sample is an order of magnitude lower than that of
In terms of the $\sigma_{\text{GB}}/\sigma_{\text{Bulk}}$ ratios, the contribution of GB conductivity is larger in the La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ sample. As shown in Table 3, the effective activation energy ($E_a$) for the bulk conductivity of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ have higher values compared to La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$, which indicates the negative effect of the sintering additive on the transfer of charge carriers. At the same time, the $E_a$ values for GB conductivity are comparable.

**Figure 12.** Temperature dependences of the proton, hole, and oxygen ion partial conductivities (a) and proton mobilities (b) of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ and La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ samples.

**Figure 13.** EIS results for La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ and La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ ceramics: (a) impedance spectra at 350 °C, (b) equivalent schemes, (c) temperature dependences of the bulk and GB conductivities, (d) $\sigma_{\text{GB}}/\sigma_{\text{Bulk}}$ ratios.
4. Discussion

Despite the fact that the homogeneity region of La$_{1-x}$Ba$_x$ScO$_{3-\delta}$ solid solutions is located in a wide range up to $x \sim 0.4$ [15,31], an increase in the Ba content already leads to a significant decrease in the ceramic density in the $x \sim 0–0.1$ concentration range (Figure 2). We considered two strategies for obtaining dense La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ ceramics: increasing the sintering temperature and introducing a sintering additive. It is understood that the sintering additive should promote both sintering due to a decrease in the material’s melting temperature at the GBs and the incorporation of the dopant into the crystal lattice due to a decrease in carbonization of the Ba in the grains surface.

The production of dense La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ ceramics without a sintering additive becomes possible only by high-temperature sintering in a vacuum at 1800 °C. In this case, large grains with a size of 7.1 ± 1.2 µm are formed (Figure 4c). The phase and chemical composition of the material correspond to the nominal ones thanks to the use of sacrificial coating powder, which prevents the evaporation of components, primarily Ba. In addition, no structural transitions were found in La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ up to 900 °C, according to HT-XRD analysis (Figure 9).

In the case of the Co$_3$O$_4$ sintering additive in La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$, the XRD and SEM results give us complex data. As SEM-EDX analysis in Figure 7b shows, the addition of 0.5 wt% Co$_3$O$_4$ in La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ results in the release of a small amount of Sc$_2$O$_3$, which is not detected by XRD [31]. The results of XRD analysis indicate partial decomposition of the material with the formation of Ba$_2$Sc$_2$O$_5$ and BaO$_2$ phases with a total mass fraction of about 1.5 wt%. Similarly, the formation of impurity phases in Ba(Ce,Zr,Y)O$_{3-\delta}$ with Fe$_2$O$_3$ and NiO sintering additives was observed in a number of works [36,55–57]. EDX analysis of the cross sections does not detect these phases, which may be due to their small size and uniform distribution. A similar situation was obtained by Shakel et al. [56] for BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ with NiO sintering additive, indicating that even transmission electron microscopy does not detect impurity phases in the form of individual grains. The XPS results in Figure 8 indicate that the Co content on the grain surface of the La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ material is negligible, confirming that Co atoms diffuse into the bulk of the grains. In addition, a noticeable part of Ba is displaced to the surface of the grains, which reduces its concentration in the grain volume. Thus, this should lead to a decrease in the concentration of oxygen vacancies formed when La is replaced by Ba in accordance with Equation (1). However, the actual concentration of Ba in the volume of the La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ sample grains corresponds to 0.048 according to EXD of the ceramics’ cross-sections (Table 2), which indicates a small contribution of Ba segregation towards the GBs.

A small amount of 0.5 wt% Co$_3$O$_4$ additive cannot explain the significant decrease in the ionic conductivity of the material, as well as the water uptake, only due to the binding of Ba to the Co. In addition, an increase in the Ba dopant concentration at a constant of Co$_3$O$_4$ sintering additive concentration leads to an increase in the precipitation of the Sc$_2$O$_3$ phase (Figure S3). The general stoichiometry of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ is obviously violated when the sintering additive is introduced, which leads to partial decomposition of the material, in particular, the formation of Ba-enriched phases. Recently, Huang et al. [35] listed a number of effects from the introduction of a NiO sintering additive into BaZrO$_3$-type materials. Violation of the cationic stoichiometry can cause the formation of cationic vacancies. Being a charged defect, cation vacancies can form associates with oxygen vacancies, which significantly reduces their mobility [56,58]. Additional trapping of oxygen vacancies is possible by Co atoms, which are embedded in Sc positions. Recent molecular

| Conductivity | LBS | LBS + Co |
|--------------|-----|---------|
| Bulk         | 0.62 eV | 0.89 eV |
| GB           | 0.98 eV | 0.95 eV |

Table 3. Effective activation energies of the bulk and GB conductivity of La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ and La$_{0.95}$Ba$_{0.05}$ScO$_{3-\delta}$ + 0.5 wt% Co$_3$O$_4$ ceramics.
dynamics modeling confirms the possibility of the association of Co with oxygen vacancies in La$_{1-x}$Sr$_{0.1}$Sc$_{1-y}$Co$_y$O$_{3-δ}$ [59]. Thus, some of the oxygen vacancies that form in accordance with Equation (1) and are directly related to the Ba dopant concentration may be associated with other defects and not participate in the oxygen ionic conductivity or water uptake (Equation (2)).

The reduced oxygen vacancy content obviously reduces the saturation limit during hydration ($x_{sd}$). As Figure 9 shows, $x_{sd}$ noticeably decreases from 0.048 for the sample without the sintering additive to 0.018 for the sample with the sintering additive. Apparently, it leads to a significant deterioration in proton transport (Figure 12a). It is fair to assume that Co atoms are partially included in the Sc site of the La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ crystal lattice, displacing part of the Sc atoms and forming the La$_{0.95}$Ba$_{0.05}$Sc$_{1-γ}$Co$_y$O$_{3-δ}$ phase. Since Co can have an oxidation state of either +2 or +3, it can serve as a source of additional holes. The transfer of electron holes to oxygen atoms will lower the 'basicity' of oxygen sites [60]; in other words, it reduces the effective negative charge on oxygen atoms. This assumption is directly confirmed by the fact that the value of the standard enthalpy of hydration for La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ + 0.5 wt% Co$_3$O$_4$ ($\Delta H_{hydr} = -62$ kJ mol$^{-1}$) becomes more positive compared to La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ ($\Delta H_{hydr} = -85$ kJ mol$^{-1}$), and thus, hydration becomes less favorable. This effect also leads to an increase in the mobility of protons in La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ + 0.5 wt% Co$_3$O$_4$ compared to La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ (Figure 12b). On the other hand, Kim et al. [61] mention a decrease in the mobility of protons when Ni is introduced into BaZr$_{0.8}$Y$_{0.2}$O$_{3-δ}$, which can be caused by the trapping of protons near Ni atoms.

The introduction of Co in La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ leads to a slight decrease in the negative contribution of the GB resistance (Figure 13d). As well, the effective activation energy of GB conductivity for La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ (0.98 eV) is higher than for La$_{0.95}$Ba$_{0.05}$ScO$_{3-δ}$ + 0.5 wt.% Co$_3$O$_4$ (0.95 eV). The positive effect of the introduction of sintering additives was previously also mentioned by the authors [62–64] for Ba(Ce,Zr)O$_3$-based materials with NiO, CuO, ZnO, Co$_3$O$_4$ sintering additives and is associated simply with an improvement in the contact between grains. Some authors [65,66] explained the decrease in the GB resistance by pointing to an increase in the concentration of charge carriers in the space charge layers and with lower potential transfer barrier. Most likely, this is facilitated by an increase in the transport numbers of holes (Figure 12a). The negative effect on the specific GB conductivity of Ba(Zr,Y)O$_3$ with the NiO additive [56,67] is associated with the blocking of ion transfers through the grain boundaries, whereas in our case, no such effect is observed.

5. Conclusions

The Ba dopant in La$_{1-x}$Ba$_x$ScO$_{3-δ}$ causes deterioration of ceramic sintering already at low concentrations of $x = 0.025–0.1$, leading to a sharp decrease in the ceramic density up to 76% after sintering at 1650 °C for 5 h, as well as a decrease in the average grain size from 0.97 to 0.34 μm. Two strategies have been applied for obtaining dense ceramics: high processing temperatures and the introduction of a Co$_3$O$_4$ sintering additive. The use of 0.5 wt% Co$_3$O$_4$ sintering additive, despite its low concentration, caused a number of negative consequences. The set of methods used indicates a violation of the overall stoichiometry of the material and the formation of impurity phases: Ba$_2$Sc$_2$O$_5$, BaO$_2$, and Sc$_2$O$_3$. A significant deterioration in the ionic conductivity of the material may indicate an association of cationic and oxygen vacancies, which excludes the latter from oxygen transport and water uptake. The incorporation of Co into Sc positions causes a weakening of the binding energy of oxygen with a proton due to the transfer of electron holes from Co to oxygen. This causes an increase in the enthalpy of the hydration reaction and proton mobility. Thus, the use of sintering additives for LaScO$_3$-based materials can lead to a number of negative consequences, since it significantly affects the actual concentration of the dopant and the cationic stoichiometry of the material. Highly dense ceramics (98%) can only be obtained by high-temperature sintering at 1800 °C, which also leads to a significant
increase in the average grain size to 7.08 µm. The accordance with the concentration of elements of the nominal composition is achieved by covering the materials with a protective powder of a similar composition, which, in particular, prevents Ba evaporation. The obtained electrolyte membranes demonstrate high water uptake and proton conductivity.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/membranes12111084/s1, Figure S1: Conductivity of ceramics as a function of (pO2)1/4 under wet (pH2O = 2.8 kPa) and dry (pH2O = 0.1 kPa) conditions; Figure S2: La3δ and Sc2p core-level spectra La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 and La0.9Sc0.1ScO3-δ + 0.5 wt% Co3O4 samples; Figure S3: SEM-images of the surface (a) and cross-sections (b) of La0.95Ba0.05ScO3-δ + 0.5 wt% Co3O4 and La0.8Ba0.2ScO3-δ + 0.5 wt% Co3O4 ceramics with EDX maps of cations distribution.

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