

Article

Properties of Perovskite-like Lanthanum Strontium Ferrite Ceramics with Variation in Lanthanum Concentration

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Abstract: The purpose of this work is to study the effect of lanthanum (La) concentration on the phase formation, conductivity, and thermophysical properties of perovskite-like strontium ferrite ceramics. At the same time, the key difference from similar studies is the study of the possibility of obtaining two-phase composite ceramics, the presence of various phases in which will lead to a change in the structural, strength, and conductive properties. To obtain two-phase composite ceramics by mechanochemical solid-phase synthesis, the method of the component molar ratio variation was used, which, when mixed, makes it possible to obtain a different ratio of elements and, as a result, to vary the phase composition of the ceramics. Scanning electron microscopy, X-ray phase analysis, and impedance spectroscopy were used as research methods, the combination of which made it possible to comprehensively study the properties of the synthesized ceramics. Analysis of phase changes depending on lanthanum concentration change can be written as follows: $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8 \rightarrow (\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8/\text{Sr}_2\text{Fe}_2\text{O}_5 \rightarrow (\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{Sr}_2\text{Fe}_2\text{O}_5$. Results of impedance spectroscopy showed that with an increase in lanthanum concentration from 0.10 to 0.25 mol in the synthesized ceramics, the value of the dielectric permittivity increases significantly from 40.72 to 231.69, the dielectric loss tangent increases from 1.07 to 1.29 at a frequency of 10,000 Hz, and electrical resistivity decreases from 1.29×10^8 to $2.37 \times 10^7 \Omega \cdot \text{cm}$.

Keywords: perovskites; strontium lanthanum ferrite; phase transformations; hardening; solid-phase synthesis



Citation: Borgekov, D.B.; Kozlovskiy, A.L.; Shakirzyanov, R.I.; Zhumazhanova, A.T.; Zdorovets, M.V.; Shlimas, D.I. Properties of Perovskite-like Lanthanum Strontium Ferrite Ceramics with Variation in Lanthanum Concentration. *Crystals* **2022**, *12*, 1792. <https://doi.org/10.3390/cryst12121792>

Academic Editors: Linghang Wang and Gang Xu

Received: 17 November 2022

Accepted: 8 December 2022

Published: 9 December 2022

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1. Introduction

One of the promising areas of research in the field of alternative energy is the search for new types of solid oxide fuel cells (SOFC) capable of operating at lower temperatures than classical materials. Interest in this area is due to the possibility of reducing the operating temperatures of SOFC materials, as well as great prospects for reducing the cost and energy costs [1–3]. At the same time, reducing the operating temperatures of SOFC elements will not only reduce energy consumption and increase efficiency, but first of all, increase the service life of the material [4,5].

In this regard, in the past few years, much attention has been paid to the development and testing of various hypotheses in this area of research, most of which are related to the study of the physicochemical, thermophysical, and conductive properties of various materials—candidates for SOFC [6,7]. At the same time, despite serious shortcomings in performance during operation at low temperatures, interest in these types of solid fuel cells does not weaken due to the large potential for reducing energy costs in the case of solving several issues related to the reduction of oxygen and hydrogen from cathode materials at low temperatures. One of the promising materials in this direction is perovskite or perovskite-like structures, which will serve as an alternative to traditional SOFC elements based on compounds of lanthanum strontium manganate with yttrium-stabilized zirconium dioxide. Among such materials, perovskite ceramics based on lanthanum strontium

ferrite are distinguished, the interest in which is due to their mixed type of electron-ion conductivity, as well as the possibility of effective oxygen reduction when used as cathode materials [8–11]. Interest in them is also due to the fact that the use of this class of ferrites can help reduce SOFC operating temperatures from high (800–1000 °C) to intermediate and low temperatures (400–800 °C). At the same time, a decrease in operating temperatures will make it possible to achieve an increase in the durability and stability of the SOFC material to degradation, as well as an improvement in thermal compatibility and stability of performance for a long time [11–15].

However, as is known, lanthanum strontium ferrite compounds have a wide range of composition stoichiometry variations, with a change in which there are significant changes not only in structural, but also in conducting and stoichiometric properties [16,17]. In this connection, studies in this direction, related to the study of the influence of stoichiometry, as well as changes in the phase composition under various synthesis conditions, have been very relevant in recent times, since the results of such studies will not only provide new data on the properties of these perovskite compounds, but also answer a number of questions related to both the phase composition effect on the electrochemical and conductive properties, and the resistance of ceramics to external influences. At the same time, variation in stoichiometry and, consequently, phase composition can be due to both synthesis processes and changes in their conditions, and variations in the initial components during the creation of perovskites [18–20].

Based on the foregoing, the main aim of this work is to consider the effect of lanthanum concentration (La) change during the synthesis of perovskite-like ceramics based on strontium ferrite on phase formation and subsequent changes in the conductive and thermophysical parameters.

2. Experimental Part

The synthesis of perovskite-like ceramics based on lanthanum-doped strontium ferrite compounds was carried out using a mechanochemical solid-phase synthesis method.

Mechanochemical synthesis was carried out using a variation in the molar ratio of the initial SrCO_3 , $\text{FeSO}_4 \times 7\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3$ components according to the chosen scheme: $(0.5 - x/2) \text{SrCO}_3$: $(0.5 - x/2) \text{FeSO}_4 \times 7\text{H}_2\text{O}$: $x \text{La}(\text{NO}_3)_3$, where x of the $\text{La}(\text{NO}_3)_3$ component ranged from 0.10 to 0.25 mol. After mechanochemical grinding, the resulting mixtures were subjected to thermal annealing at a temperature of 1000 °C. According to the classical chemical reactions of thermal decomposition of the initial components used to obtain perovskite ceramics, when these components are heated, gaseous compounds are released in the form of CO_2 , SO_2 , NO_2 , and H_2O . The isolation of these compounds with the formation of simple Fe_2O_3 , La_2O_3 , SrO oxides, as a rule, occurs at temperatures above 700 °C. In this case, the formation of complex perovskites occurs through the interaction of Fe_2O_3 , La_2O_3 , SrO oxides.

Mechanochemical solid-phase synthesis was carried out using the PULVERISETTE 6 classic line planetary mill (Fritsch, Idar-Oberstein, Germany). Grinding was carried out at a speed of 400 rpm for 1 h. After grinding, the resulting mixtures were annealed at a temperature of 1000 °C for 5 h; the samples were cooled to room temperature for 24 h while they were inside the furnace.

The study of morphological features and changes in the shape and size of the grains of the synthesized ceramics depending on the La concentration was carried out using the scanning electron microscopy method implemented on a Jeol 7500 F microscope (Jeol, Tokyo, Japan). The element distribution isotropy in the structure of ceramics was determined using the method of energy dispersive analysis.

The phase composition and structural parameters of the synthesized ceramics depending on the component concentration, as well as with dopant variation, were estimated using the X-ray diffraction method implemented on a D8 Advance ECO powder diffractometer (Bruker, Berlin, Germany). The phase composition was determined using the PDF-2(2016)

database. Refinement of the parameters and determination of the degree of crystallinity were carried out in the Diffraction v.4.2 program code.

Measurement of current–voltage characteristics using the cyclic voltammetry method was carried out at room temperature ($T = 25\text{ }^{\circ}\text{C}$) using a potentiostat-impedance analyzer PalmSens4+ (PalmSens BV, Houten, The Netherlands). Polished copper plates of the same area were used as electrodes (1 cm^2). Impedance spectroscopy of the obtained samples was performed on a HIOKI IM3533-01 LCR meter on compressed powders. Silver glue was used to create electrical contacts. To measure the cyclic current–voltage characteristics and impedance characteristics, the resulting powders were pressed into pellets. All measurements were performed in five parallels to determine the measurement error, standard deviations, and also to establish the repeatability of the results obtained not only on different samples, but also when re-measuring the obtained characteristics to determine the stability. Figure 1 shows an image of powders obtained after mechanochemical solid-phase synthesis and thermal annealing, as well as after pressing to measure the impedance characteristics. To measure the characteristics, the samples were pressed into pellets 10 mm in diameter and 0.5 mm thick. The obtained samples after pressing were subjected to thermal drying at a temperature of $60\text{ }^{\circ}\text{C}$; for 2 h to evaporate the polyvinyl alcohol used for pressing.



Figure 1. Image of perovskites before and after the pressing procedure.

3. Results and Discussion

One of the most common ways to obtain perovskite or perovskite-like ceramics is the method of mechanochemical solid-phase synthesis, whose condition variation makes it possible to obtain, with a high controllable accuracy, structures with specified parameters or phase composition in any volume, which can be used quite well in the future when scaling up this technology and manufacturing ceramics on an industrial scale. At the same time, the variation of the initial mixture composition also makes it possible to obtain different compositions of ceramics, with a uniform distribution of elements over the volume.

Figure 2 below shows SEM images of the studied perovskite-like ceramics depending on the lanthanum concentration, reflecting changes in the morphological features of the ceramics. The SEM images are made on the obtained powders after thermal annealing. As can be seen from the data presented, in the case of a lanthanum concentration of 0.10 mol, ceramics are coarse-grained structures, rhomboid or pyramidal in shape, surrounded by spherical or near-spherical particles, the size of which varies in the range of 150–300 nm. At the same time, analysis of the obtained images showed that quite large grains are also found in ceramics, the size of which exceeds 1–1.5 μm , which are surrounded by smaller spherical particles; in the aggregate, this structural phenomenon is close to a dendrite-like structure with high porosity. An increase in the lanthanum concentration to 0.15 mol in the structure of ceramics also leads to the formation of dendrite-like structures; however, with a slight decrease in the size of large particles, as well as the formation of double triple grain boundaries between particles.

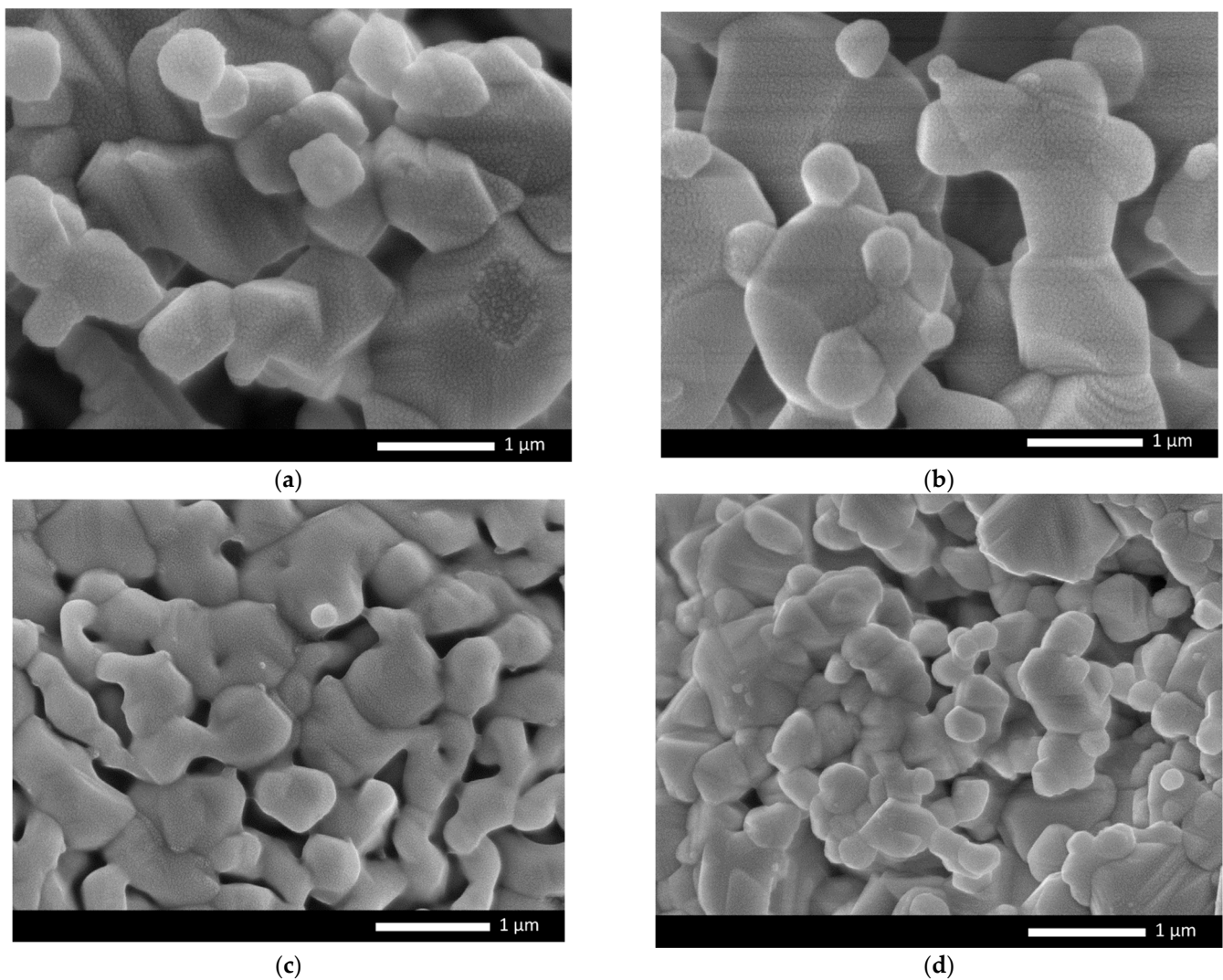


Figure 2. SEM images of synthesized perovskite-like powders as a function of La concentration: (a) 0.10 mol; (b) 0.15 mol; (c) 0.20 mol; (d) 0.25 mol.

With an increase in the lanthanum concentration to 0.20 mol and higher, a significant change in the morphological features of the synthesized perovskite-like ceramics is observed, which consists of the formation of a fine-grained structure that forms clusters of grains, as well as the absence of large grains, which were found at lower lanthanum concentrations. At the same time, the concentration of pores with a change in morphology and a decrease in grain size becomes much lower, and in the case of a concentration of 0.25 mol. It is also worth noting that a change in concentration leads to an increase in the degree of homogeneity of grain sizes, due to a decrease in the contribution of coarse-grained inclusions.

Table 1 presents the results of energy-dispersive analysis of the studied samples, reflecting the ratio of elements. As can be seen from the data presented, an increase in the lanthanum concentration for synthesis leads to an increase in its content in the composition of the samples under study.

A change in morphological features, as a rule, can be associated with a change in the phase composition of the samples as a result of the initialization of phase transformation processes with a change in the ratio of component concentrations in ceramics. The figure shows the results of X-ray phase analysis of the studied samples depending on the concentration of lanthanum, reflecting the processes of phase transformations with a change in the component concentration. The general view of the presented diffraction patterns, in

addition to the change in the phase composition, which is reflected in the formation of new diffraction reflections with a change in the lanthanum concentration, also shows changes in the degree of crystallinity of the synthesized ceramics (see the data in Figure 3).

Table 1. Data of energy-dispersive analysis.

Concentration of Element, at. %	Concentration, mol			
	0.10	0.15	0.20	0.25
La	2.2 ± 0.3	4.6 ± 0.5	7.3 ± 0.5	10.4 ± 0.9
Sr	21.2 ± 1.6	20.1 ± 1.5	17.8 ± 1.1	16.4 ± 1.7
Fe	17.3 ± 1.2	16.6 ± 1.3	16.4 ± 1.8	15.3 ± 1.4
O	59.3 ± 2.2	58.7 ± 2.5	58.5 ± 2.6	57.9 ± 2.3

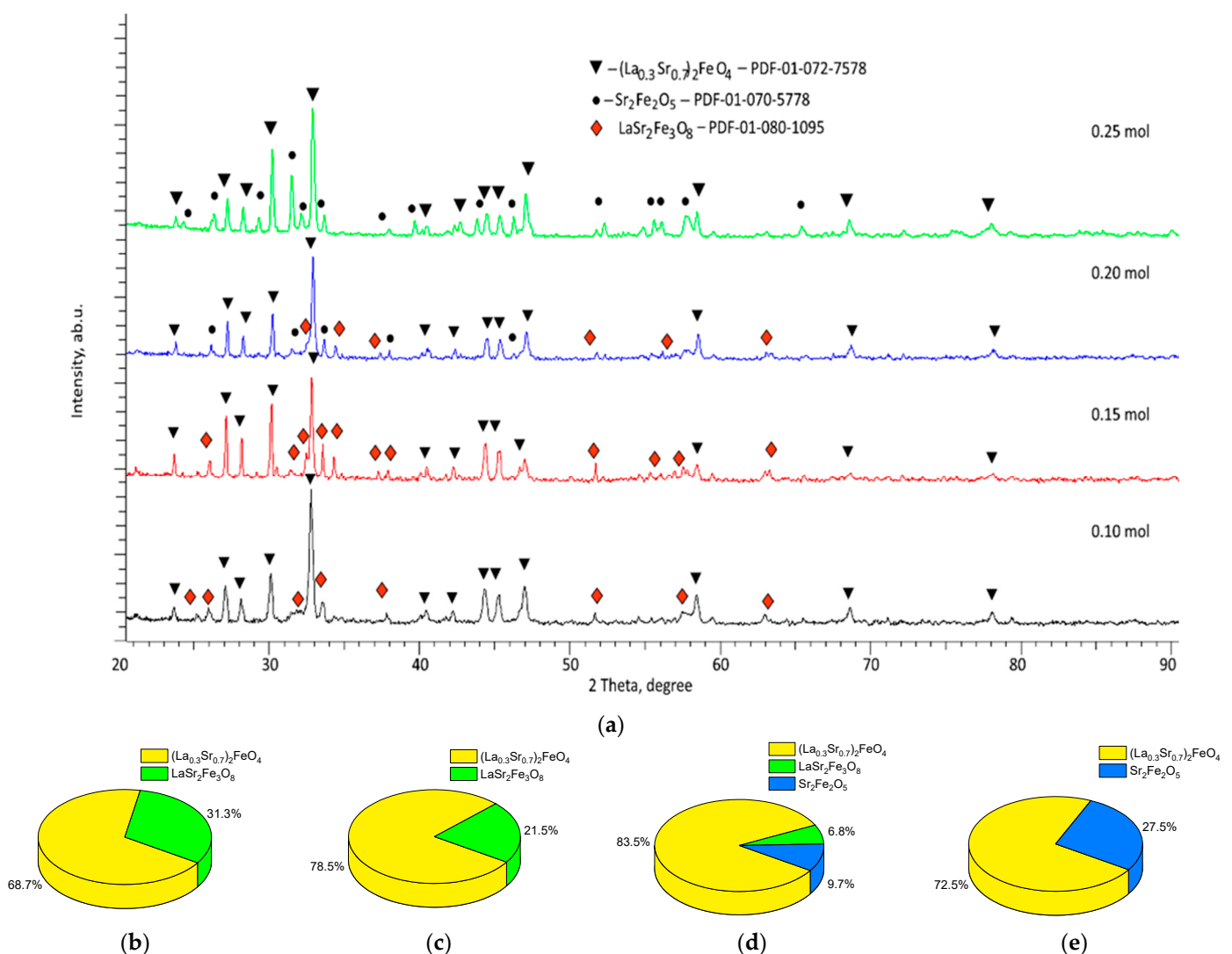


Figure 3. (a) X-ray diffraction patterns of synthesized ceramics based on lanthanum strontium ferrite depending on the lanthanum concentration; phase diagrams of the synthesized ceramics depending on the lanthanum concentration: (b) 0.10 mol; (c) 0.15 mol; (d) 0.20 mol; (e) 0.25 mol.

According to the phase composition analysis of the samples, it was found that at lanthanum concentrations of 0.10–0.15, the main contribution is made by the tetragonal $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4$ phase, as well as the orthorhombic $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase, the content of which decreases with an increase in lanthanum concentration from 31.3% to 21.5%. These

phases are structures of substituted strontium ferrite, in which part of the strontium ions are replaced by lanthanum, in which partial substitution of Sr^{2+} for La^{3+} leads to the formation of structures with mixed iron valence, as well as the possible formation of oxygen vacancies. The contributions of each phase were estimated by determining the areas of reflections with subsequent calculation of their weight contribution in terms of 100%. At the same time, as can be seen from the analysis of the shape of diffraction reflections and their relationship with the area characteristic of an amorphous-like or disordered structure, a decrease in the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase contribution leads to an increase in structural ordering (see the data in Figure 4).

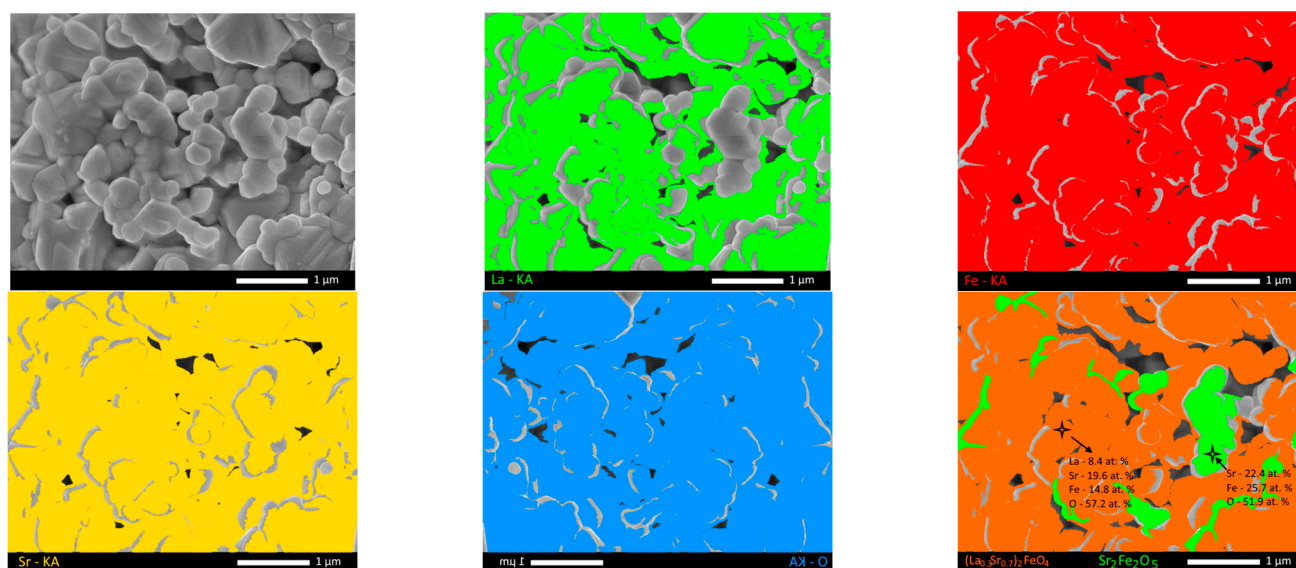
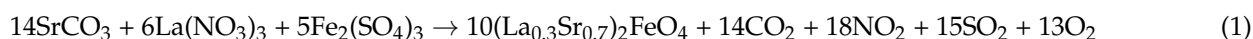


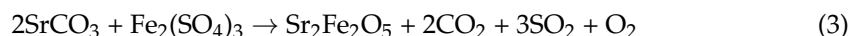
Figure 4. Mapping results of the studied powders with La concentration equal to 0.25 mol.

In the case of a change in concentration from 0.15 mol to 0.20 mol, in addition to the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase displacement, which is expressed in a decrease in the intensity of diffraction reflections characteristic of it, the appearance of reflections characteristic of the orthorhombic $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase (brownmillerite-type structure) was observed on the diffraction pattern, the presence of which indicates phase transformation processes occurring as a result of a change in the concentration of components, as well as the $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4$ phase dominance. At the same time, analysis of the shape of reflections indicates that these phase transformations are accompanied by an increase in the degree of crystallinity and a decrease in distortions and deformations in the structure of ceramics. In the case of a lanthanum concentration of 0.25 mol, the complete displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase and the formation of two-phase ceramics, which has a high degree of crystallinity of more than 90% is observed. The presence of amorphous inclusions determined from the crystallinity degree values may be due to incompletely formed phases during thermal annealing, as well as transitional inclusions in the form of oxide compounds formed during the decomposition of the initial components.

Analyzing the obtained X-ray phase analysis data of the synthesized ceramics, depending on the lanthanum concentration, the following phase conversion scheme can be formed:

$(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8 \rightarrow (\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8/\text{Sr}_2\text{Fe}_2\text{O}_5 \rightarrow (\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{Sr}_2\text{Fe}_2\text{O}_5$. The basic equations of chemical reactions that occur as a result of the thermal annealing of samples with the formation of those observed by X-ray diffraction can be written as follows (Equations (1)–(3)):





At the same time, Equations (1) and (2), according to the data of X-ray phase analysis, are typical for $\text{La}(\text{NO}_3)_3$ concentrations equal to 0.10–0.15 mol, and reactions Equations (1) and (3) for $\text{La}(\text{NO}_3)_3$ concentrations equal to 0.20–0.25 mol. The formation of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase in the form of individual inclusions was also confirmed by the results of mapping the samples, according to which, in the structure of the annealed powders, the presence of small grains not containing lanthanum is observed, and the analysis of the elemental composition of these grains shows the ratio of Sr:Fe:O elements close to the stoichiometric ratio for the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase (see the data in Figure 4).

Table 2 presents the data on the change in the crystal lattice parameters depending on the La concentration. The density of ceramics was calculated using the method of X-ray diffraction analysis based on changing the structural parameters and volume of the crystal lattice, as well as taking into account the contribution of various phases, and for comparison, the results of measuring the density of ceramics obtained using the Archimedes method for pressed samples are given.

Table 2. Structural parameter data.

Phase	Concentration, mol			
	0.10	0.15	0.20	0.25
$(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4$ — Tetragonal I4/mmm(139)	$a = 3.8561 \pm 0.0026 \text{ \AA}$, $c = 12.6995 \pm 0.0018 \text{ \AA}$	$a = 3.8661 \pm 0.0029 \text{ \AA}$, $c = 12.7069 \pm 0.0021 \text{ \AA}$	$a = 3.8548 \pm 0.0024 \text{ \AA}$, $c = 12.6746 \pm 0.0032 \text{ \AA}$	$a = 3.8495 \pm 0.0025 \text{ \AA}$, $c = 12.6572 \pm 0.0032 \text{ \AA}$
$\text{LaSr}_2\text{Fe}_3\text{O}_8$ — Orthorhombic Pmma(51)	$a = 5.5214 \pm 0.0027 \text{ \AA}$, $b = 11.9101 \pm 0.0023 \text{ \AA}$, $c = 5.6127 \pm 0.0024 \text{ \AA}$	$a = 5.5333 \pm 0.0029 \text{ \AA}$, $b = 11.8751 \pm 0.0023 \text{ \AA}$, $c = 5.6226 \pm 0.0021 \text{ \AA}$	$a = 5.5279 \pm 0.0024 \text{ \AA}$, $b = 11.8588 \pm 0.0022 \text{ \AA}$, $c = 5.6127 \pm 0.0024 \text{ \AA}$	-
$\text{Sr}_2\text{Fe}_2\text{O}_5$ —Orthorhombic, Icmm(74)	-	-	$a = 5.6575 \pm 0.0032 \text{ \AA}$, $b = 15.5625 \pm 0.0023 \text{ \AA}$, $c = 5.5216 \pm 0.0034 \text{ \AA}$	$a = 5.6519 \pm 0.0023 \text{ \AA}$, $b = 15.5533 \pm 0.0025 \text{ \AA}$, $c = 5.5118 \pm 0.0034 \text{ \AA}$
Density (method of X-ray diffraction analysis), g/cm ³	5.673	5.694	5.654	5.535
Density (Archimedes method), g/cm ³	5.564	5.523	5.602	5.504

According to the presented data, it can be seen that the density values obtained by both methods are in fairly good agreement, which indicates a rather low porosity in the case of pressed samples. In this case, the change in density has a pronounced dependence on the phase composition, and a slight decrease in density is due to the lower density for the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase in comparison with the density of $\text{LaSr}_2\text{Fe}_3\text{O}_8$.

An analysis of the change in the crystal lattice parameters depending on the lanthanum concentration indicates that the phase transformation processes are accompanied by the crystal lattice rearrangement, with partial substitution of ions at the sites, as well as their intrusion into interstices, which leads to deformation processes of stretching and volume expansion, which are clearly visible when the concentration increases from 0.10 to 0.15 mol. Additionally, an increase in the parameters for a given concentration range can be explained by the formation of an orthorhombic $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase in the structure. Displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase at concentrations of 0.20 mol and higher leads to a decrease in the crystal lattice parameters, which indicates structural ordering, which is also clearly visible when analyzing the shape of diffraction reflections and calculating the crystallinity degree parameter, the results of which change depending on the lanthanum concentration are shown in Figure 5. Additionally, during analysis of the deformation contributions to the change in structural parameters, as well as their distortion, it was found that the

$\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase displacement leads to a more than threefold decrease in the defect fraction concentration in the ceramic structure, which can also contribute to a change in its conducting and electrochemical properties.

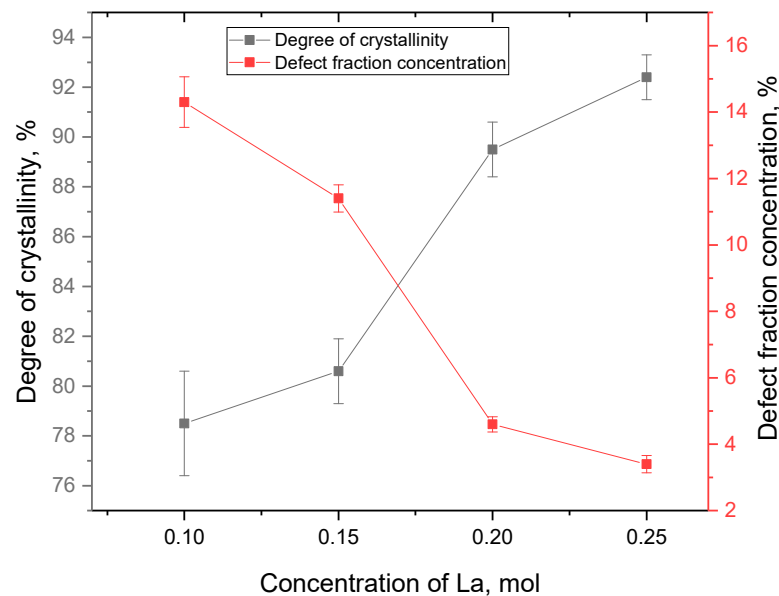


Figure 5. Results of changes in the crystallinity degree and the defect fraction concentration in the composition of ceramics with variation of the components.

The obtained results of the change in the phase composition and structural perovskite-like ceramics depending on the concentration of the initial components are in good agreement with previous similar studies of strontium lanthanum ferrites obtained by various methods. Thus, for example, the results of the change in the phase composition with an increase in lanthanum concentration with the formation of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase with the brownmillerite structure, as well as the displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase and its replacement by the $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4$ phase, are in good agreement with the results of studies [21,22] in which similar ceramics were obtained by the sol-gel method from strontium, iron, and lanthanum nitrates annealed at a temperature of 400–1300 °C. However, in contrast to works [21–23], these phase transformation processes occur at lower sintering temperatures (1000 °C), and it also makes it possible to control both size effects and phase concentration. In comparison with single-phase ceramics [24], the results of the degree of crystallinity are much higher for two-phase ceramics, which can be further used to increase the strength and stability of ceramics.

Figure 6 shows the results of cyclic voltammetry of the studied ceramic samples depending on the change in the lanthanum concentration in the composition. As can be seen from the data presented, in the case of the dominance of $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4$ and $\text{LaSr}_2\text{Fe}_3\text{O}_8$ in the composition of phases, the nature of the change in the current–voltage curves is described by a straight line, which has a close to ohmic nature of the change in the conductive properties. At the same time, a change in the lanthanum concentration from 0.10 to 0.15 mol does not lead to significant changes in the current–voltage characteristics, as well as a change in the conductivity nature. In turn, the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase displacement with the subsequent formation of an orthorhombic $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase leads to an increase in the slope of the current–voltage curve, as well as the appearance of hints of a transition from an ohmic nature of the conductivity to a semiconductor one. In the case of the complete displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase at lanthanum concentration of 0.25 mol with the formation of two-phase $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{Sr}_2\text{Fe}_2\text{O}_5$ type ceramics, a sharp change in the conductivity nature is observed, with the dominance of the semiconductor nature in the region from −4 to 4 V, as well as a decrease by more than 2–3 orders of magnitude of the resistivity. Such a change in the conductive properties of ceramics may be due to the fact

that the presence of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase, which has a dielectric nature, leads to an increase in resistance, while its displacement with the subsequent formation of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase leads to a change not only in the resistance value, but also in the conductivity nature from ohmic to semiconductor. Such a change in the conductivity type with a change in the phase composition of perovskite-like ceramics, followed by the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase displacement and the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase formation, indicates that ionic conductivity begins to predominate in the structure.

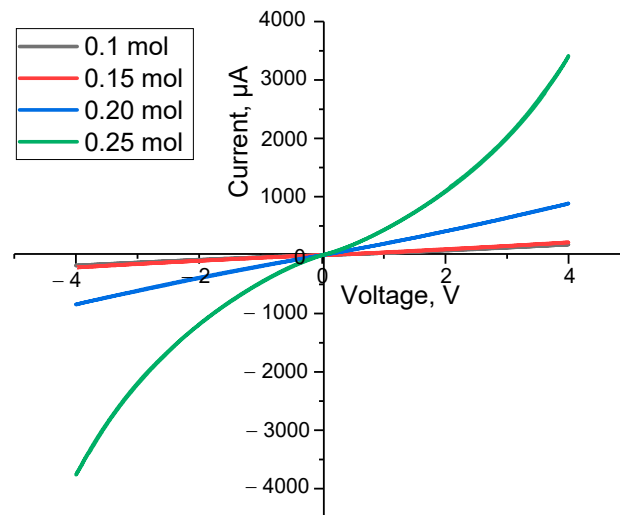


Figure 6. Graphs of cyclic current–voltage characteristics of synthesized ceramics depending on the lanthanum concentration.

Figure 7 shows the results of changes in the electrochemical characteristics of the synthesized ceramics depending on the lanthanum concentration when they are used as an air electrode of SOFC element at a temperature of 550 °C. The fabrication of an SOFC cell was carried out according to the standard technology for obtaining three-layer devices, where $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ powder at a concentration of 0.20 g pressed with synthesized ceramics and nickel foam was used as an electrolyte, and synthesized ceramics and nickel foam ($\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_{2-\delta}$) were used as an air electrode. Nickel foam was also used as an anode. After pressing, the resulting devices were annealed at a temperature of 600 °C for 4 h in an argon atmosphere to compact the SOFC. The performance of the cells was demonstrated in a humidified hydrogen fuel 3% H_2O and air with atmospheric oxidizers, at a drift rate of H_2/air of $100 \pm 5\%$ mL/min.

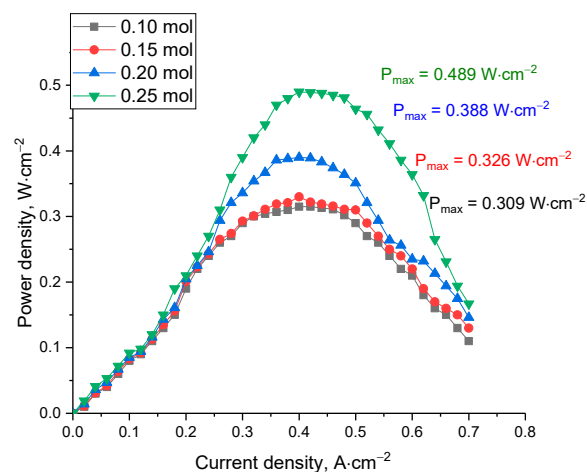


Figure 7. Electrochemical characteristics: current density–specific power (I–P) characteristic curves.

As can be seen from the data presented, the maximum value of specific power is achieved at an open circuit voltage of approximately 1.1–1.15 V; it varies from $0.309 \text{ W}\cdot\text{cm}^{-2}$ to $0.489 \text{ W}\cdot\text{cm}^{-2}$ depending on the phase composition of the ceramics. At the same time, in the case when the $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4$ phase dominates in the composition of the ceramics, the power value changes insignificantly from 0.309 to $0.326 \text{ W}\cdot\text{cm}^{-2}$ with a decrease in the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase contribution from 31 to 22%. Formation of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase in the composition of ceramics leads to an increase in $P_{\max}$ to $0.388 \text{ W}\cdot\text{cm}^{-2}$, and subsequent displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase leads to an increase in $P_{\max}$ to $0.489 \text{ W}\cdot\text{cm}^{-2}$, which, in comparison with the values for samples of the $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase composition, is an increase in power by more than 50%.

Figure 8 shows the Cole–Cole plot and the frequency dependences of the complex permittivity plotted for the obtained samples. Figure 8a shows that the dependences $Z''(Z')$ for samples with 0.10, 0.15, and 0.20 do not represent a semicircle characteristic of a parallel RC chain [24]. This can be explained by the influence of polarization at the ceramic/electrode interface, as well as by a more complex electrical equivalent circuit describing the structure of the resulting ceramic. The data from the Cole–Cole diagrams correlate with the measurements of I–V dependences and electrochemical characteristics, since, as shown in the I–V and I–P dependences, with an increase in the mole fraction of $\text{La}(\text{NO}_3)_3$, the electrical power increases, the electrical resistance decreases, and the value of the impedance Z' , Z'' decreases [25]. The frequency dependences of the dielectric permittivity show (Figure 8b) that in the frequency range of 2–200 kHz, the values of the real part and the imaginary part of the permittivity decrease significantly with increasing electric field frequencies. In the low-frequency region, the processes of interfacial polarization significantly increase the values of ϵ' , ϵ'' , since the electric charge has time to fully accumulate at the semiconductor/dielectric interface. Such interfaces most likely arise due to the pronounced semiconductor properties of the $(\text{La}_{0.3}\text{Sr}_{0.7})\text{FeO}_4$ phase.

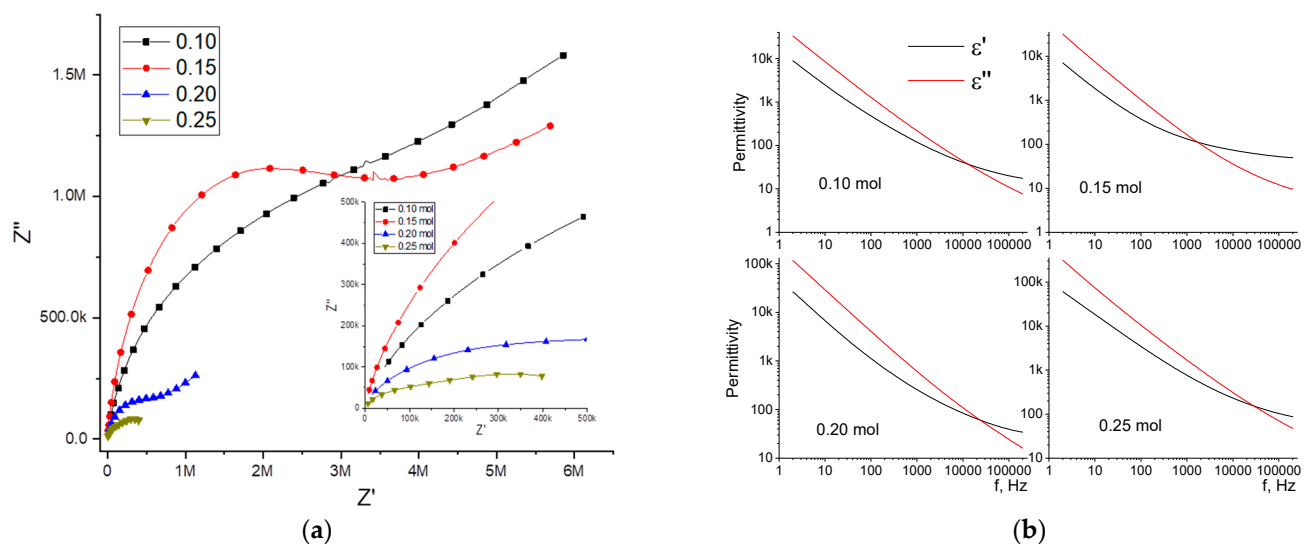


Figure 8. Cole–Cole diagrams $Z''(Z')$ (a) and frequency dependences of the complex permittivity (b).

For example, it was shown in [26] that the system $\text{La}_{1-x}\text{Nd}_x\text{SrFeO}_4$ with the space group m has a resistivity of $77.62 - 4 \times 10^2 \Omega\cdot\text{cm}$ for the values $x = 0.0, 0.3, 0.6, 0.9$. Conductivity in $\text{La}_{1-x}\text{Nd}_x\text{SrFeO}_4$ is explained by the mechanism of hopping polaron electrical conductivity [26] with a low activation energy of the process 0.2–0.3 eV. The decrease in electrical resistance is associated with a decrease in the antiferromagnetic interaction when Fe^{3+} cations are replaced by Dy^{3+} cations, which leads to an increase in electron mobility. Semiconductor properties of LaSrFeO_4 are also reported in other works, where the electrical resistivity is in the range of 2.4×10^3 – $10^7 \text{ Ohm}\cdot\text{cm}$ [27–29]. LaSrFeO_4 with an excess of Sr creates holes and p-type conduction in $\text{Fe}^{4+}/\text{Fe}^{3+}$ pairs when La^{3+} is replaced by the Sr^{2+}

cation. In the case of oxygen deficiency, $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs appear in ceramics, generating electrons and n-type conductivity. From Table 3, it is evident that the electrical resistivity ρ_{DC} of the obtained samples is higher than in the above-mentioned works [27–30]. This is due to the presence of a phase with high electrical resistance. The $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase in the synthesized ceramics acts as an insulator.

Table 3. Comparison of permittivity ϵ' , dielectric loss tangent $\tan \delta = \epsilon''/\epsilon'$ at 10 Hz, 10,000 Hz and DC resistance ρ_{DC} .

Mol.	ϵ' (10 Hz)	ϵ' (10,000 Hz)	$\tan \delta$ (10 Hz)	$\tan \delta$ (10,000 Hz)	$\rho_{\text{DC}} \times 10^7, \Omega \cdot \text{cm}$	Conductivity, S/cm
0.10	2461 ± 50	40.7 ± 2.0	3.4 ± 0.2	1.1 ± 0.1	12.9 ± 0.4	0.07
0.15	1848.6 ± 80	73.7 ± 5.0	4.0 ± 0.3	0.5 ± 0.1	13.1 ± 0.4	0.07
0.20	6727 ± 110	84.1 ± 6.0	4.0 ± 0.3	1.3 ± 0.2	2.9 ± 0.2	0.34
0.25	$18,382 \pm 120$	231.6 ± 11.0	4.3 ± 0.2	1.2 ± 0.3	2.4 ± 0.3	0.41

From the analysis of the I-V dependences, it can be seen that in the samples obtained, the highest current value is observed where the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase is present and the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase is absent. This allows us to conclude that the electrical resistivity of $\text{Sr}_2\text{Fe}_2\text{O}_5$ is the lowest of all the phases that make up ceramics, and its presence significantly reduces the value of the electrical resistance. This is also evidenced by the fact that the shape of the I-V curve changes from a linear dependence to an exponential dependence characteristic of a metal/semiconductor structure. Among the scientific publications for the $\text{Sr}_2\text{Fe}_2\text{O}_5$ compound, data on the electrical properties are scarce, but a low electrical resistance is reported, for example, in [31]. The presence of this component largely determines the dielectric properties of the resulting ceramics. The effective value of the permittivity, conductivity, electrical resistivity, and loss tangent are determined by the concentration of the phases that make up the ceramic.

From Table 3, which compares the dielectric parameters at fixed frequencies and DC conductivity, it can be seen that the largest values of ϵ' and the smallest values of ρ_{DC} are characteristic of samples with the presence of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase.

Table 3 presents the results of the change in the conductivity value for the studied ceramics, obtained by evaluating the Cole–Cole diagrams $Z''(Z')$, which reflect the following. The displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase from the structure with the subsequent formation of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase in the structure leads to an increase in specific conductivity by approximately an order of magnitude, which indicates a change in the nature of conductivity in ceramics, associated not only with a change in the phase composition, but also with a change in the charge transfer mechanisms.

4. Conclusions

The paper presents the results of changes in the structural, conductive, and electrochemical properties of perovskite-like ceramics based on lanthanum strontium ferrite, depending on the variation of the components. An analysis of morphological tests showed that an increase in the lanthanum concentration leads to a change in the morphology and grain sizes associated with their crushing and the formation of close-packed ceramics. In this case, as shown by X-ray phase analysis, the change in morphology is due to the processes of phase transformations of the $(\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8 \rightarrow (\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{LaSr}_2\text{Fe}_3\text{O}_8/\text{Sr}_2\text{Fe}_2\text{O}_5 \rightarrow (\text{La}_{0.3}\text{Sr}_{0.7})_2\text{FeO}_4/\text{Sr}_2\text{Fe}_2\text{O}_5$ type. The results of impedance spectroscopy showed that with an increase in the concentration of lanthanum from 0.10 to 0.25 mol in synthesized ceramics, the dielectric constant value increases significantly from 40.72 to 231.69, the dielectric loss tangent increases from 1.07 to 1.29 at a frequency of 10,000 Hz, and there is a decrease in specific electrical resistance from 1.29×10^8 to $2.37 \times 10^7 \Omega \cdot \text{cm}$. These changes in the dielectric characteristics are associated with phase transformations in ceramics, in which the ratios between phases with different

electrical characteristics change. An analysis of electrochemical measurements showed that the displacement of the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase with the subsequent formation of the $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase in the structure leads to an increase in the specific power by more than 50% compared to two-phase ceramics containing the $\text{LaSr}_2\text{Fe}_3\text{O}_8$ phase.

Author Contributions: Conceptualization, D.I.S., D.B.B., A.T.Z., R.I.S. and A.L.K.; methodology, M.V.Z. and A.L.K.; formal analysis, M.V.Z., R.I.S., D.I.S. and A.L.K.; investigation, M.V.Z., D.I.S. and A.L.K.; resources, A.L.K.; writing—original draft preparation, review, and editing, D.B.B., R.I.S., D.I.S. and A.L.K.; visualization, A.L.K.; supervision, A.L.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (No. AP13068071).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare that they have no conflict of interest.

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