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The temperature dependence investigation of the frequency dispersion of the electrical properties of lithium-iron spinel doped with La, Y

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The temperature-frequency dependences of the electrical characteristics of $Li_2 Fe_{2.5-x} Me_x O_4$ (Me = La; Y, x = 0.01; 0.03; 0.05) spinels synthesized by the «sol-gel» autocombustion technology were obtained by the method of impedance spectroscopy in the temperature range of 298-473 K.

Based on their analysis, the main mechanisms of conductivity of these materials in the studied temperature range were identified: hopping and activation, which are competing. The effect of doping lithium-iron spinels with rare-earth metal impurities on these conductivity mechanisms has been investigated. It has been established that the presence of impurities in small concentrations in the synthesized samples significantly decreases their conductivity mainly due to destruction of the hopping mechanism of electronic conductivity.

Keywords: impedance spectroscopy, spinel, frequency dispersion of electrical conductivity, activation energy, Arrhenius curves, hopping mechanism of conductivity.

Introduction

Nowadays, due to their dielectric and magnetic properties, spinel ferrites are widely used in radio engineering, radar, communication systems, and as memory carriers in computers. At the same time, the ability of such materials to the process of intercalation-deintercalation of lithium ions in their structure allows them to be considered as a promising material for the manufacture of the matrix of cathodes of portable lithium current sources [1].

The electrical properties of ferrites strongly depend on the method of synthesis, preparation conditions, chemical composition, cation distribution and microstructure of the material. The doping method is one of the most common in chemistry and technology as a way to control the structure of complex oxides and create new functional materials. The determining factor is the ability of the dopant ion to form an isomorphic substitution in the matrix structure of host [2].

The work [3] showed the prospects of replacing the traditional lithium-manganese spinel in lithium-ion batteries with a more stable lithium-iron oxospinel, more widely studied as a magnetic material. The similarity of the structures of lithium-manganese and lithium-iron spinel and the content of lithium ions in them were the reason for the attempt to use the latter polycrystalline system as a cathode material.

However, as shown in [1], its significant drawback is the low degree of electrochemical deintercalation of lithium from the $Li_{0.5}Fe_{2.5}O_4$ matrix due to the presence of Fe^{2+} ions in the structure, which restore part of the "guest" Li^+ ions to the atomic state and, thus, exclude the latter from an electrochemical process. Therefore, studies of the effect of modifying the electrophysical characteristics of lithium-iron spinel by isovalent replacement of iron ions with trivalent metal ions, including aluminum ions, have become relevant. Aluminum-doped lithium-iron spinels-ferrites with the general formula $Li_{0.5}Fe_{2.5-x}Al_xO_4$, synthesized by ceramic technology, have attracted the attention of researchers as stable ferrite materials widely used in modern technological systems [4,5].

The morphology, phase content, crystal structure of the spinel phase of the synthesized Al-substituted lithium-iron spinels depending on the composition and mode of heat treatment at the final stage of synthesis, and their electrophysical characteristics were investigated in works [6,7]. Research in [8] of the temperature dependence of the conductivity of the synthetic material showed that in the temperature range lower than 475 K, the electronic component of the conductivity of these disordered systems dominates, which can be realized using two mechanisms: hopping and activation. It was shown in work [9] that in the region of temperatures higher than 475 K in the synthesized $Li_{0.5}Fe_{2.5-x}Al_xO_4$ ceramics, the Li^+-ion mechanism of conductivity becomes predominant. In this work the temperature-frequency dependences of Li^+-ion conductivity at different values of the aluminum content were interpreted on the basis of a generalized phenomenological model of charge transfer in superionic conductors [10]. Thereat the values of the concentrations of conductivity Li^+ ions, their macroscopic and microscopic mobilities were obtained in the entire studied temperature range for different values of the aluminum content in the synthesized samples.

In recent years, in order to expand the range of electrophysical properties of lithium-iron spinels, which can be useful in various fields of technology, in addition to isovalent substitution of iron ions with aluminum ions, attempts are being made to substitute iron ions with ions of other elements. In this regard, the doping of lithium-iron spinels with ions of rare earth metals may be a promising direction. A number of works [11-13] have been published in scientific journals in which the structure, morphology and electromagnetic properties of several nanocrystalline iron spinels doped with rare earth metals using the «sol-gel» synthesis technology are investigated.

Atoms and ions of rare earth elements, with a constant valence of +3, have uncompensated spin moments in *f*-orbitals [14]. The ions of different rare earth elements are quite close in their chemical properties, since their outer electron shells are identical - they all have the *5s²5p⁶* configuration. The radii of trivalent ions gradually decrease from 1,11 Å for cerium (Ce) to 0.94 Å for ytterbium (Yb) as we move from one element of the group to another. This phenomenon is called lanthanoid compression, thanks to which it is possible to control the properties of crystals containing rare earth elements to a large extent by selecting the required radius of the trivalent ion for the crystals.

Ions of rare earth elements have pronounced magnetic properties. The difference between the magnetic properties of the ions of the group of rare-earth elements and the transition (*3d*) metals is that the spin moments of the *4f*-electrons are «hidden» in the inner electron shell of the rare-earth element the radius of which is about 0.3 Å. In view of this, ferrites, synthesized on the basis of rare earth elements and widely used in technology, have a high electromagnetic Q factor. The reason for this is that the connection of the active «magnetic subsystem» that is excited in ferrites by an external electromagnetic field with thermal phonons is weak, that is, a kind of "shielding" of the magnetically active subsystem from thermal fluctuations occurs.

The purpose of this work is to study the temperature-dependent frequency dispersion of conductive and dielectric properties of lithium-iron spinels doped with two representatives of rare earth metals - lanthanum and yttrium, synthesized by the technology of «sol-gel» autocombustion.

I. Research methodology

The procedure of «sol-gel» autocombustion synthesis, which used for the synthesis of the samples, was as follows: for each composition, according to the formula, the necessary amounts of starting compounds were calculated, which were selected as crystal hydrates of iron nitrates $Fe(NO_3)_3 \cdot 9H_2O$, lithium $LiNO_3$, lanthanum $La(NO_3)_3 \cdot 9H_2O$ and yttrium $Y(NO_3)_3 \cdot 9H_2O$. Citric acid acted as a chelating agent, and an aqueous ammonia solution was added to adjust the pH level of the reagent solution. Metal nitrates were dissolved in distilled water until complete dissolution with constant stirring with a magnetic mixer with the addition of citric acid. Ammonia solution (10%) was added dropwise to the precursors solution to adjust the required pH level ($\approx$ 7). The resulting solution was kept in a drying cabinet at a temperature of 343 K until the water was completely removed. After that, the dry gel was placed in an oven and heated to a temperature of 523-553 K at which the mixture ignited, and the final product was formed. For conducting impedance studies, briquettes were created by pressing the obtained powder with the addition of a 10% solution of polyvinyl alcohol (PVA). The obtained samples with a diameter of 1 cm and a height of about 0.4 cm were subjected to sintering at a temperature of 873 K for 4 hours in an air atmosphere with slow cooling.

Conductive and dielectric characteristics of the synthesized compounds were calculated on the basis of experimental impedance spectra obtained on Autolab PGSTAT 12/FRA-2 spectrometer in the frequency range of 0.01 Hz - 100 kHz and the temperature range of 293-473 K. Temperature recordings were carried out with isothermal exposure every 20 K.

II. The results of the experiment and their discussion

The structure, morphology, phase composition, electrophysical properties of pure and aluminum-substituted lithium-iron spinels synthesized by the ceramic method have already been studied in detail in a number of research works [6-10]. Analysis of the temperature dependences of direct current conductivity in works [8,9] indicates the dominance of electronic conductivity in these ceramics in the temperature range of 295-475 K, and in the temperature range higher than 475 K, a cationic mechanism of conductivity appears and begins to dominate as the temperature increases, the activation energy of which lies within 0.9−1.4 eV.

Electronic conductivity can be realized using two mechanisms: hopping and activation [8]. Activation conduction is carried out by the drift in the electric field of free charge carriers generated in the conduction band

either from the valence band or from the donor levels. The hopping mechanism of electrical conductivity in these ceramics is mainly realized by the hopping of an electron between ions of the same element (in this case, these are ions Fe^{2+} and Fe^{3+}), which can be in more than one valence state, randomly distributed in crystallographically equivalent positions of the lattice [15]. In the temperature range of 295-350 K, the hopping mechanism dominates, the activation energy of which lies within the range of 0.10-0.14 eV, and in the range of 350-475 K, the activation mechanism dominates, the activation energy of which is approximately equal to 0.35 eV [8].

First, we will analyze the impedance temperature-frequency spectra of pure lithium-iron spinels synthesized by the technology of «sol-gel» autocombustion and compare them with the above-mentioned results of the analysis of the impedance temperature-frequency spectra of these compounds synthesized by the ceramic method [16].

The impedance spectrum of pure lithium ferrite obtained by the "sol-gel" autocombustion technology in the entire investigated temperature range is presented in Figure 1.
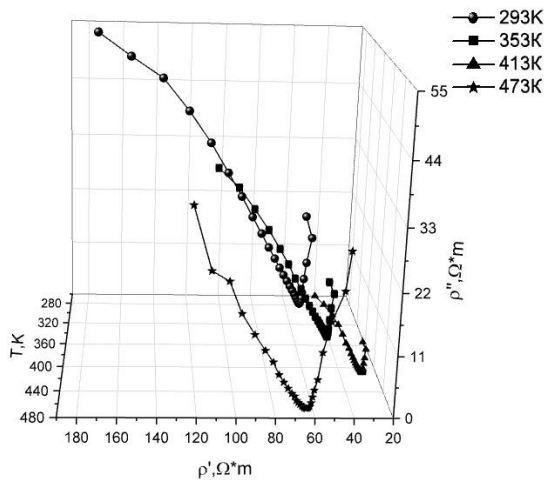

Fig. 1. Nyquist diagrams for $Li_{0,5}Fe_{2,5}O_4$ polycrystal at different temperatures.

Taking into account the dimensions of the sample, the measured resistances were reduced to their specific values. A characteristic feature of Nyquist diagrams is that they are of the same type for all temperatures and consist of the arcs of two semicircles (truncated on the high and low frequency sides, as they are outside the working frequency range), describing the high-frequency and low-frequency regions of the spectrum. As the temperature increases, the radii of the high-frequency arcs of the hodographs decrease except for the last one, which corresponds to the temperature T = 473 K, which means that the resistance of the sample decreases as the temperature increases from 293 K to 413 K, and then begins to increase. In addition, it should be noted that the values of the resistances of the samples synthesized by the "sol-gel" autocombustion technology are 2-3 orders of magnitude lower than the values of the resistances of the samples synthesized by the ceramic method.

The impedance spectrum of this type can be modeled by an equivalent circuit consisting of an active resistance and two successive RC circuits (Figure 2).
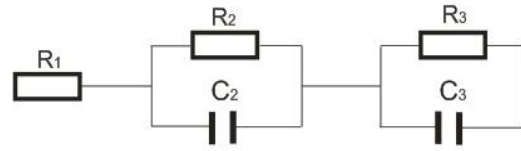

Fig. 2. Equivalent circuit to the Nyquist diagram.

According to the proposed model, the substance contains inclusions from grains and intergrain boundaries. The first component of the circuit corresponds to the ohmic part of the resistance (R1) of the sample which is independent of frequency. Objects modeled electrically as separate RC elements can be grains of the polycrystal (R_2C_2) and intergrain boundaries (R_3C_3).

Table 1 shows the values of specific conductivity σ_0 and dielectric permeability ε_0 at direct current for each component of the equivalent circuit.

Table 1.

Component	Parameters	
	$\sigma_0, S \cdot m^{-1}$	ε_0
1	0.019	–
2	0.029	$2.59 \cdot 10^7$
3	0.012	$5.53 \cdot 10^8$

Dielectric permeabilities obtained directly from calculations using equivalent circuits agree quite well with direct measurements at low frequencies, as can be seen from Figure 3. The reason that the dielectric constant ε' of the studied samples increases strongly with decreasing frequency and reaches very large values, in our opinion, is the accumulation of electric charges transferred by Li^+ ions near the blocking electrodes and grain boundaries due to volume-charge (migratory) polarization, which can occur due to the presence of free crystallographic positions of spinels and the high mobility of lithium cations. The presence of a volume charge significantly increases the electrical capacity of the capacitor, and therefore the value of ε'.

To study the conductivity mechanisms of the synthesized samples of lithium-iron spinel, we will consider the frequency dispersion of the real part of the specific conductivity (σ') in the studied temperature range. Figure 4 presents the dependences of σ'(ω) obtained from Nyquist diagrams at different temperature values.

Analysis of the σ'(ω) curves presented in Figure 4 shows:

1) at all temperatures of the studied range, in the region of low frequencies from 0.0628 s^{-1} to 10^2–10^3 s^{-1}, the conductivity of spinel increases, and then in the interval 10^3–10^5 s^{-1} it almost does not change (increases very weakly) and, starting from the frequency $1.2 \cdot 10^5$ s^{-1}, decreases;

2) with an increase in temperature from 293 K up to 433K, the conductivity of spinel at all frequencies increases, and then, after reaching a temperature of 433K, it drops sharply.

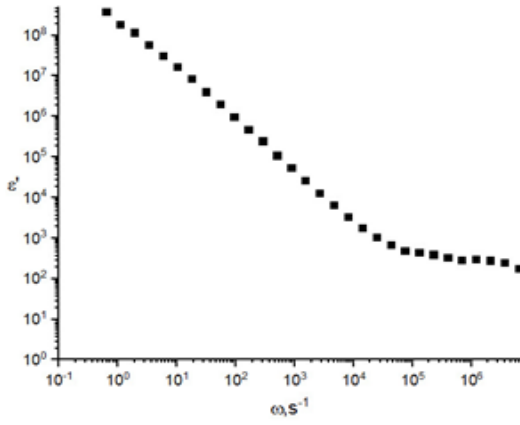This behavior of conductivity depending on temperature and frequency may indicate the dominance in

Fig. 3. Experimental dependence of the dielectric permeability of $Li_{0.5}Fe_{2.5}O_4$ spinel on the frequency at the temperature T = 293 K.

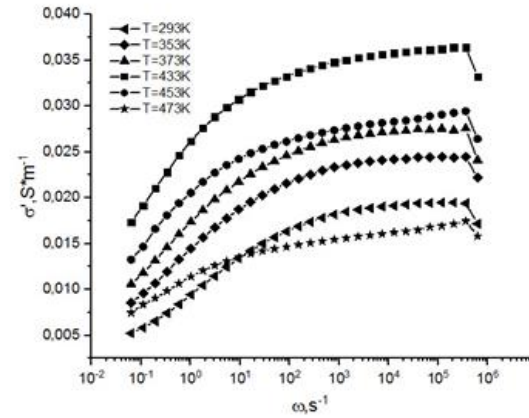**Fig. 4.** Frequency dependences of the real part of the specific conductivity $\sigma'(\omega)$ of $Li_{0.5}Fe_{2.5}O_4$ spinel at different temperature values.

the synthesized sample of the electronic hopping mechanism of conductivity, which is realized through chain percolation processes $Fe^{+2} - e^- \leftrightarrow Fe^{+3}$ in octapositions of lithium oxoferrite spinel. At low frequencies, these processes are hindered by polarization processes caused by the displacement of lithium ions under the action of an electric field within single crystal grains. As the frequency increases, the influence of these processes decreases, and when it exceeds the frequency of natural vibrations of lithium ions, which is in the range of 10^2-$10^3 s^{-1}$, the conductivity remains constant until reaching frequencies that exceed the frequency of natural vibrations of the valence electron in the ion Fe^{+2} ($\sim 10^5 c^{-1}$). In this case, with increasing frequency, the time of electron movement in the direction of the field decreases and, therefore, an increasing number of such electrons do not reach the crystallographically equivalent positions of the lattice, where Fe^{+3} ions are located, so the conductivity decreases. Using Mott's theory, it is possible to calculate the parameters characterizing the hopping mechanism of conductivity [15].

The value of the specific conductivity of the samples at direct current σ_0 at different temperatures was determined by the diagram
$\sigma' - (\sigma'' - \varepsilon_0\varepsilon_\infty\omega)$ ($\varepsilon_0 = 8.85 \cdot 10^{-12} F/m$, $\varepsilon_\infty -$ the value of dielectric permeability at high frequencies, which was found from the Cole-Cole diagram $\varepsilon'' - \varepsilon'$). The dependence of σ_0 on temperature is presented in Figure 5.

The significant direct current conductivity of the obtained samples in comparison with the samples of pure and aluminum-substituted lithium-iron spinel obtained by the ceramic method [16] can be due to the fact that in them the single-crystal grains are quite closely adjacent to each other and the current flows along the surfaces of the contacting grains , which is evidenced by the photo of the microstructure of the sample, which is presented in Fig. 6a, and the high capacity of the grain boundary region ($C_3 \sim 10^{-4} F$).

A hopping mechanism of conductivity has an activation character because there is a local displacement of the electron cloud in the direction of the applied field and additional polarization occurs. The activation energy of this mechanism is low and, as shown in [8], does not exceed 0.15 eV for aluminum-substituted lithium-iron
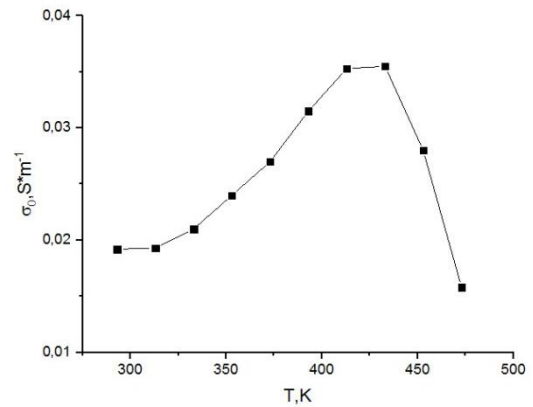
spinel ceramics.

Fig. 5. Dependence of the direct current conductivity of $Li_{0.5}Fe_{2.5}O_4$ spinel on temperature.

The evidence of the realization of the activation mechanism of conductivity is the presence of a straight section on the Arrhenius curve (the temperature dependence of the specific conductivity of the direct current presented in the coordinates $ln\sigma_0\left(\frac{1}{T}\right)$). Activation conductivity is described by the equation:

$$\sigma = \sigma_\infty \cdot e^{-\frac{\Delta E}{2kT}},$$

where ΔE is the activation energy of the conduction process, k is the Boltzmann constant, and σ_∞ is the value of the specific conductivity at $T \to \infty$. Then the activation energy is determined by the formula:

$$\Delta E = \frac{T_1 T_2 ln\frac{\sigma_1}{\sigma_2}}{2k(T_1 - T_2)},$$

where temperatures T_1, T_2 and specific conductivities σ_1, σ_2 correspond to the coordinates of the edges of the rectilinear section on the Arrhenius curve.

On the Arrhenius curve for the sample of lithium-iron spinel synthesized by us using the "sol-gel" autocombustion technology, presented in Figure 7, two
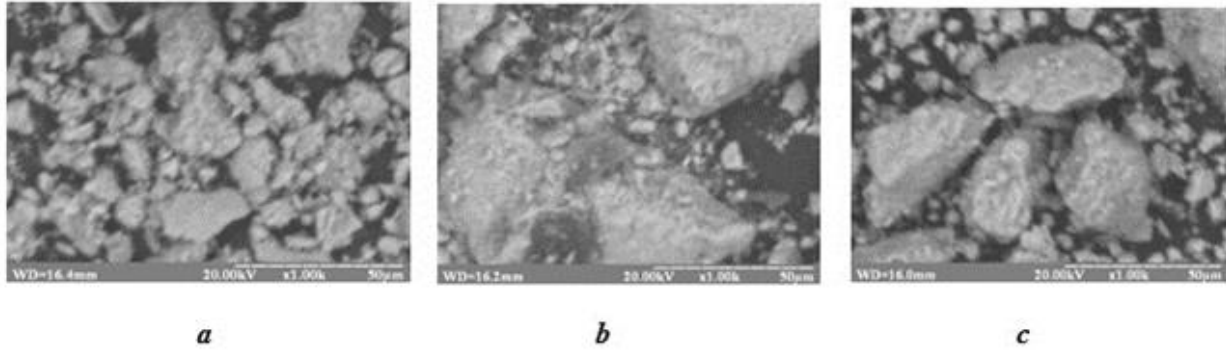
Fig. 6. SEM image of the structure: a − $Li_{0.5}Fe_{2.5}O_4$; b − $Li_{0.5}Fe_{2.5-x}La_xO_4$ (x = 0.03); c − $Li_{0.5}Fe_{2.5-x}Y_xO_4$ (x = 0.03).

sections with different slopes of the approximating straight line can be distinguished. In the temperature interval of $293\,K \leq T \leq 313\,K$, which corresponds to the first section, with a slight slope of the approximating straight line, a hopping conduction mechanism is realized, the activation energy of which is equal to 0.04 eV.
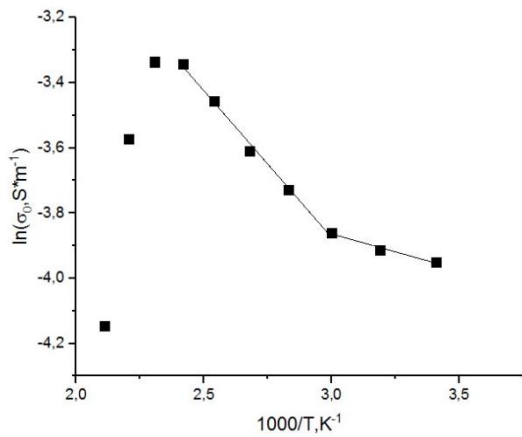

Fig. 7. Arrhenius curve for the sample of $Li_{0.5}Fe_{2.5}O_4$ spinel.

As the temperature increases, the hopping mechanism breaks down and, starting at a temperature of 313 K, the activation mechanism becomes dominant up to a temperature of 433 K, when almost all valence electrons, leaving the Fe^{+2} ions under the influence of an external electric field, do not enter due to thermal vibrations of lattice nodes into Fe^{+3} ions, and become free, entering the internodal space (that is, from the donor levels of the band within which the hopping mechanism is realized, they pass into the conduction band). Thus, in the temperature range $313\,K \leq T \leq 433\,K$, which corresponds to the second section with a greater slope of the approximating straight line, an activation mechanism is realized, the activation energy of which is equal to 0.16 eV. As can be seen from Figure 5, starting from a temperature of 433 K, there is a close to linear decrease in specific conductivity at direct current with increasing temperature, that is, due to the depletion of the donor band in which the valence electrons of Fe^{+2} ions are located, the metallic character of the conductivity is observed in the synthesized samples.

Let us now investigate how the replacement of iron ions with ions of two representatives of rare earth elements: lanthanum (La) and yttrium (Y) affects the electrical properties of lithium-iron oxospinels. Lanthanum and yttrium ions in chemical compounds can exist only in trivalent states. Most ions of the group of rare earth elements have pronounced magnetic properties due to the presence of electrons with unpaired spins in the $4f$ shell. They are paramagnetic. In lanthanum, with which this group of elements begins, the $4f$ shell is empty and therefore the La^{+3} ion is diamagnetic. As a result of the replacement of iron ions Fe^{+2} and Fe^{+3} in lithium oxospinels (the magnetic moments of which are equal to $5.4\mu_B$ and $5.9\mu_B$, respectively) by ions of various lanthanides, which have different magnetic moments ranging from 0 in La^{+3} to $10.6\mu_B$ in Dy^{+3}, their magnetic properties will vary quite a lot. However, their electrical properties are similar, since all lanthanides have the same structure of outer electron shells and they differ only in ionic radii. Therefore, the results of the study of the influence of lanthanum doping of lithium-ferrite oxospinel on its electrical properties can be generalized to cases of doping with other lanthanides. Trivalent yttrium ions Y^{+3}, like lanthanum La^{+3} ions, are diamagnetic, but unlike them, they have a completely filled outer electron shell of $4s^2 4p^6$ and, therefore, a much smaller ionic radius.

Figure 8 presents experimental Nyquist diagrams for samples of $Li_{0.5}Fe_{2.5-x}La_xO_4$ composition with different lanthanum content.

As can be seen from this figure, the specific complex resistance of the samples increases strongly with an increase in the content of lanthanum in them. Therefore, the direct current specific conductivity of the samples strongly decreases with increasing lanthanum content. Table 2 shows the values of direct current conductivity and dielectric permeability of the components of the equivalent electrical circuit presented in Figure 2 for the $Li_{0.5}Fe_{2.5-x}La_xO_4$ sample with x = 0.03.

The obtained values are consistent with the experimental frequency dependences of the real part of the dielectric permeability of $Li_{0.5}Fe_{2.5-x}La_xO_4$ for different values of the lanthanum content in the samples presented in Figure 9, from which it follows that as the lanthanum content in the samples increases, their dielectric permeability at low frequencies decreases.

Figure 6b shows a photograph of the microstructure of $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel for x = 0.03. A comparative analysis of this photograph with the photograph of the microstructure of pure lithium-iron spinel presented in Figure 6a shows that doping it with lanthanum leads to a
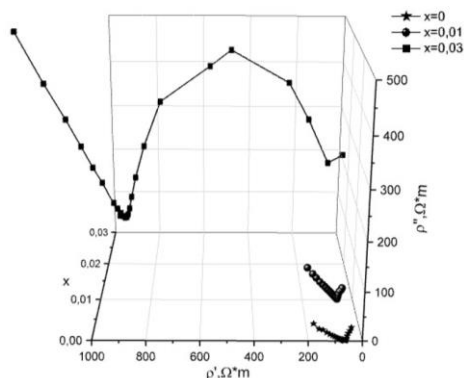
Fig. 8. Nyquist diagrams for the specific values of the complex impedance $\rho''(\rho')$ at the temperature T = 293 K for the studied samples of the composition $Li_{0.5}Fe_{2.5-x}La_xO_4$ with x = 0; 0.01; 0.03.

Table 2.

Component	Parameters	
	$\sigma_0, S \cdot m^{-1}$	ε_0
1	0.0023	–
2	0.0011	$1.58 \cdot 10^4$
3	0.0004	$7.50 \cdot 10^7$

violation of the homogeneity of the microstructure of the synthesized samples, i.e. to an increase in the dispersion of the sizes of single-crystal grains and an increase in the distance between them. Thereat as follows from the comparison of the data in Table 2 with the data in Table 1 and the analysis of the experimental curves $\varepsilon'(\omega)$ for different values of the lanthanum content presented in Figure 9, the specific conductivities and dielectric permeability at direct current, which correspond to the region of the grains and the region of intergrain boundaries decrease, and for the region of intergrain boundaries, they decrease significantly. These experimental facts lead us to the conclusion that the vast majority of La^{+3} ions are localized in the surface layer of single-crystal grains (since their radii are much larger than the radii of iron ions and they are not able to integrate into the middle of the crystal lattice of single-crystal grains), demolishing electronic
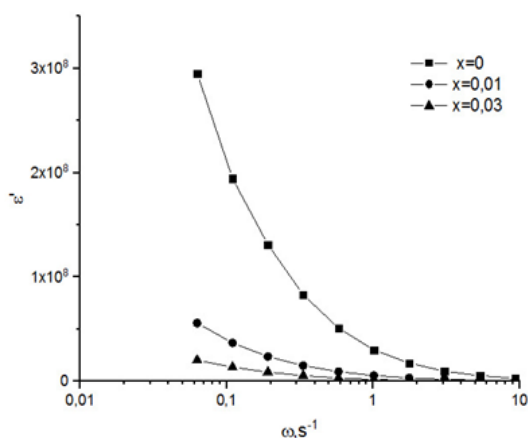
conductivity in it, which is due to the hopping mechanism. As a result, the specific conductivity of grain boundary surfaces is significantly reduced, and therefore the total specific conductivity of the synthesized samples.

A decrease in the direct current conductivity of the synthesized samples with increasing lanthanum content is shown in Figure 10, which presents the experimental temperature dependence of σ_0 for different values of the lanthanum content.

On the experimental Arrhenius curves for samples of $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel with different lanthanum content, presented in Figure 11, one can distinguish rectilinear sections that are approximated by straight lines with different angles of inclination to the 1000/T axis, that may indicate the existence of two competing electronic conduction mechanisms: hopping and activation. The activation energies of these mechanisms can be determined by the tangents of these angles.

As follows from the results of the analysis of the inclination angles of the approximating straight lines presented in Figure 11, the presence of an impurity leads to an approximately a two-fold increase in the activation energy of both the hopping mechanism (from 0.04 eV up to 0.08-0.1 eV) and the activation one (from 0.16 eV up to 0.29-0.31 eV) compared to the case of pure (without impurities) lithium-iron spinel. Thereat with an increase in the impurity content, the temperature at which the hopping mechanism is replaced by the activation one increases. This change in conduction mechanisms can be visually interpreted using a simplified scheme of energy bands presented in Figure 12. According to this scheme, in the forbidden band, at the distance of the activation energy of the donor conduction mechanism from the bottom of the conduction band ΔE_a there is a narrow band 1, which is completely filled with valence electrons, which are located on Fe^{+2} ions.

Above this band, at the distance of the activation energy of the hopping mechanism ΔE_h, there is a narrow empty band 2 in which the excited electrons do not linger and pass to the vacant energy levels of the original band 1. At low temperatures, the energy of the external electric field or thermal oscillations is sufficient only for the
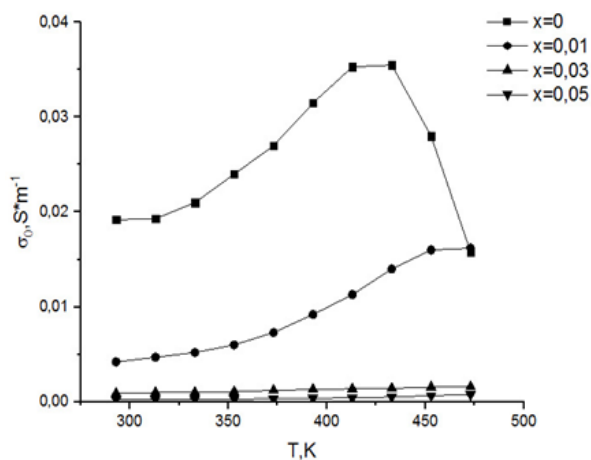

Fig. 9. Experimental dependences of the dielectric permeability of $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel on the frequency at the temperature T = 293 K and different values of the lanthanum content in the samples (x = 0; 0.01; 0.03).

Fig. 10. Experimental temperature dependences of specific conductivity at direct current $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel for different values of lan-thanum content in the samples (x = 0; 0.01; 0.03; 0.05).

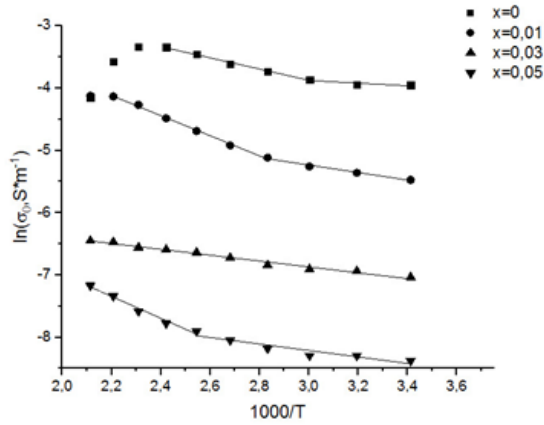**Fig. 11.** Experimental Arrhenius curves with selected straight sections for $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel samples with different lanthanum content in the samples (x = 0; 0.01; 0.03; 0.05).

Fig. 12 Scheme of electronic energy bands of $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel.

transition of electrons from band 1 to band 2. The number of electrons in band 1 is determined by the number of Fe^{+2} ions in the samples, which decreases as the number of La^{+3} impurity ions increases. The transition of electrons from band 1 to the conduction band determines the metallic character of conductivity, in which the mobility of electrons decreases with increasing temperature and the conductivity drops, which is exactly what is observed in Figure 10 for the case of a sample of pure lithium-iron spinel.

As follows from Figure 13, in contrast to $Li_{0.5}Fe_{2.5}O_4$ spinel, the specific conductivity of $Li_{0.5}Fe_{2.5-x}La_xO_4$ (x = 0.01) spinel at all frequencies increases with increasing sample temperature, and in the frequency range $\omega > 10^5 s^{-1}$ a maximum appears, which, in our opinion, can be associated with the appearance and growth of Li^+-ion conductivity against the background of a sharp decrease in electronic conductivity due to the hopping mechanism. The Li^+-ion mechanism of conductivity of lithium-iron spinel doped with aluminum was studied in detail by us on the basis of the generalized Jonscher model for superionic conductors [9].

The effect of replacing iron ions with yttrium ions Y^{+3} on the electrical properties of lithium-iron spinels has the same character as the effect of lanthanum ions La^{+3}. Figure 6c shows a photograph of the microstructure of $Li_{0.5}Fe_{2.5-x}Y_xO_4$ spinel for x = 0.03, from which it can be seen that the yttrium impurity, as well as the lanthanum impurity, leads to heterogeneity of the structure of the synthesized samples, which is characterized by a dispersion of grain sizes and an increase in the average distance between them.

Figure 14 shows the experimental temperature dependences of the direct current conductivity σ_0 for different values of the yttrium content in the samples. The presence of an yttrium impurity in the synthesized samples reduces their conductivity significantly more than the presence of a lanthanum impurity.

The analysis of the experimental Arrhenius curves for $Li_{0.5}Fe_{2.5-x}Y_xO_4$ spinel presented in Figure 15 shows that already with the content of yttrium impurity with x = 0.01 in the entire studied temperature range only the activation donor conduction mechanism is possible.
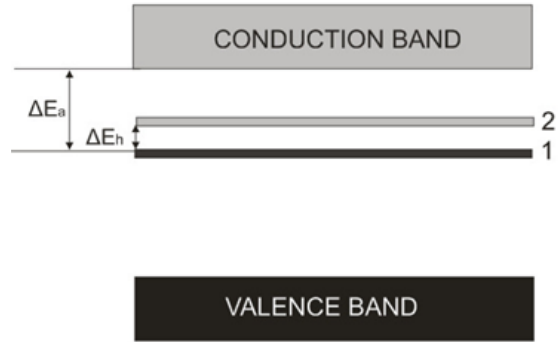
It is realized in the temperature range $293K \leq T \leq 413K$ with activation energy $\Delta E_a = 0.15 - 0.16$ eV. This means that yttrium ions due to their smaller radius are better embedded in the crystal lattice of the surface layer of lithium-iron spinel grains than lanthanum ions.
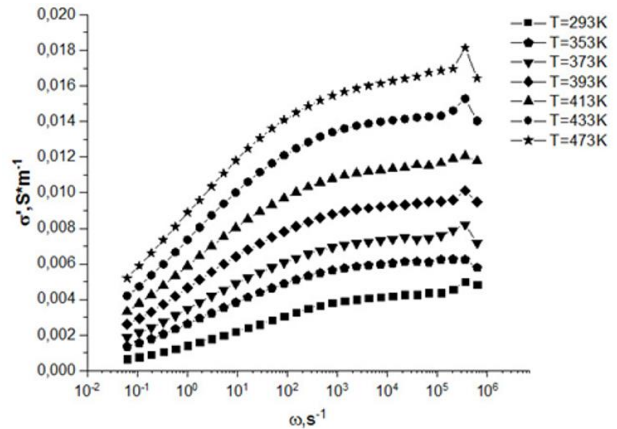

Fig. 13. Frequency dependences of the real part of the specific conductivity $\sigma'(\omega)$ of $Li_{0.5}Fe_{2.5-x}La_xO_4$ (x = 0.01) spinel at different temperature values.

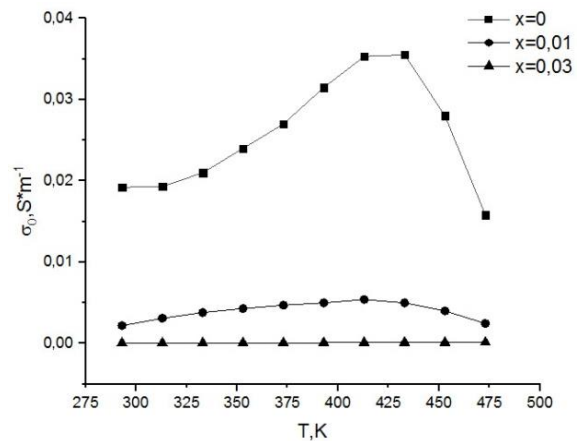**Fig. 14.** Experimental temperature dependences of specific conductivity at direct current $Li_{0.5}Fe_{2.5-x}Y_xO_4$ spinel for different values of yttrium content in the samples (x = 0; 0.01; 0.03).

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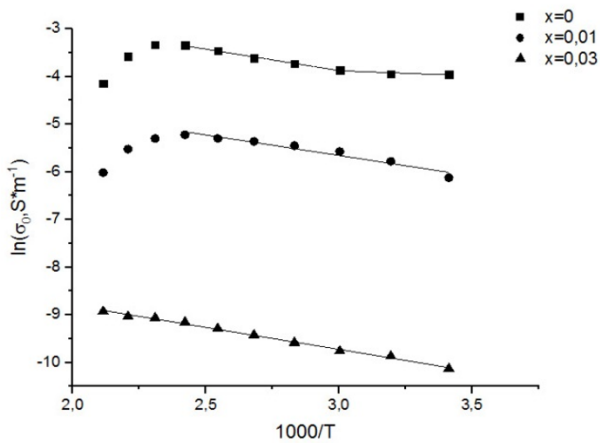**Fig. 15.** Experimental Arrhenius curves with selected straight sections for $Li_{0.5}Fe_{2.5-x}Y_xO_4$ spinel samples with different yttrium content in the samples (x = 0; 0.01; 0.03).

The temperature behavior of the frequency curves of conductivity for $Li_{0.5}Fe_{2.5-x}Y_xO_4$ spinel is similar to that for $Li_{0.5}Fe_{2.5-x}La_xO_4$ spinel. Figure 16 shows the temperature-frequency dependences of the conductivity of the $Li_{0.5}Fe_{2.5-x}Y_xO_4$ spinel sample with the yttrium content corresponding to x = 0.01. From the analysis of these dependencies, it follows that:
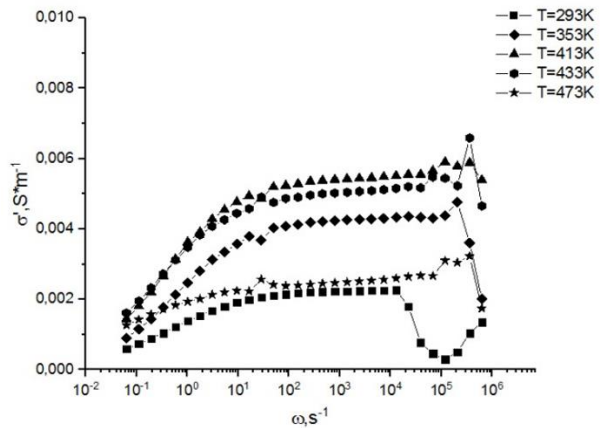

Fig. 16. Frequency dependences of the real part of the specific conductivity $\sigma'(\omega)$ of $Li_{0.5}Fe_{2.5-x}Y_xO_4$ (x = 0.01) spinel at different temperature values.

1) in the temperature range $293K \leq T \leq 413K$ there is an increase, and in the range $413K \leq T \leq 473K$ there is a decrease in conductivity at all frequencies. The decrease in conductivity with increasing temperature can be explained according to the scheme of energy bands (Figure 12) by the depletion of the donor band due to the transition of almost all electrons from it to the conduction band.

2) in the region of high frequencies $\omega \sim 10^5$Hz, the dependence of the conductivity on the frequency becomes non-monotonic, except for the curve that corresponds to the temperature $T = 293K$. This curve shows a monotonic decrease in conductivity in the frequency interval

10^4Hz $\leq \omega \leq 10^5$Hz and its growth in the frequency interval 10^5Hz $\leq \omega \leq 10^6$Hz. This behavior may indicate the appearance and growth of Li^+-ion conductivity against the background of a sharp decrease in electronic conductivity, as in the case of a lanthanum impurity.

Conclusions

The conductivity of samples of lithium-iron spinel synthesized by the "sol-gel" autocombustion technology is significantly higher than the conductivity of samples synthesized by the traditional ceramic method. This is due to the fact that the microstructure of these samples in our case is more homogeneous and the current flows along the surfaces of the contacting single-crystal grains.

In the studied temperature interval of 293 K $\leq$ T ≤ 473 K, two competing electronic mechanisms of conductivity can be realized: hopping and activation. The hopping mechanism dominates in the region of low temperatures and corresponds to the transition of electrons under the influence of an external electric field from the donor band 1 to the empty band 2 which are located in the band gap (according to the scheme of energy bands). In the region of higher temperatures, the hopping mechanism changes to an activation one, which corresponds to the transition of electrons under the influence of temperature from the donor band to the conduction band. With a further increase in temperature, the donor band is emptied and all electrons from it pass to the conduction band. Then the metallic character of conductivity is realized.

Doping lithium-iron spinel with ions of rare earth metals leads to a sharp decrease in its conductivity. The first reason for this is a violation of the homogeneity of the microstructure of the synthesized samples (an increase in the size dispersion of single-crystal grains and an increase in the distances between them), and the second one is the destruction of the hopping mechanism of conductivity (a decrease in the concentration of Fe^{+2}ions by replacing them with trivalent ions of rare earth metals, and as well as the resulting increase in the average distance between iron ions in the crystal lattice of the grain) In the case of doping lithium-iron spinel with yttrium ions, against the background of a sharp decrease in electronic conductivity in the high-frequency region of the spectrum, Li^+ ion conductivity may appear even at low temperatures.

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Дослідження температурної залежності частотної дисперсії електричних властивостей літій-залізної шпінелі, легованої La, Y

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Методом імпедансної спектроскопії отримані температурно-частотні залежності електичних характеристик $Li_2Fe_{2.5-x}Me_xO_4$ (Me = La;Y, x = 0,01; 0,03; 0,05) шпінелей, синтезованих за технологією «золь-гель» автоспалювання, в інтервалі температур 298-473 К. На основі їх аналізу виявлені основні механізми провідності цих матеріалів в досліджуваному інтервалі температур: перескоковий та активаційний, які є конкуруючими. Досліджено вплив на ці механізми провідності легування літій-залізних шпінелей доміщками рідкісноземельних металів. Встановлено, що присутність цих домішок в малих концентраціях у синтезованих зразках значно зменшує їх провідність в основному завдяки руйнуванню перескокового механізму електронної провідності.

Ключові слова: імпедансна спектроскопія, шпінель, частотна дисперсія електричної провідності, енергія активації, криві Арреніуса, стрибковий механізм провідності.