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Hopping conductivity in lithium-iron spinel doped with La, Y

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The temperature-frequency dependences of the electrical characteristics of $Li_2Fe_{2,5-x}Me_xO_4$ (Me = La; Y, x = 0; 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 293-473 K.

Based on their analysis, the main mechanisms of conductivity of these materials in the studied temperature range were identified: hopping and activation. It was shown that at low temperatures the hopping mechanism of conductivity dominates. The main parameters of hopping conductivity have been determined. The effect of doping lithium-iron spinels with rare-earth metal impurities on them has been investigated.

Keywords: impedance spectroscopy, spinel, activation energy, Arrhenius curves, hopping mechanism of conductivity, Fermi level, Mott's theory.

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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 depend significantly 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. 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 [2,3].

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 [4,5]. Research in [6] 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 [7] that in the region of temperatures higher than 475K in the synthesized $Li_{0,5}Fe_{2,5-x}Al_xO_4$ ceramics, the Li^+-ion mechanism of conductivity becomes predominant.

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 ions of other elements. In this regard, the doping of lithium-iron spinels with ions of rare earth metals may be a promising trend. A number of papers [8-10] 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.

The work [11] investigated the temperature-frequency dependences of the conductivity of $Li_2Fe_{2.5-x}Me_xO_4$

(Me = La; Y, x = 0; 0.01; 0.03; 0.05) spinels synthesized by the "sol-gel" autocombustion technology, in temperature range 293-473 K. On the basis of their analysis, it was determined that the main mechanisms of conductivity of these materials in the studied temperature range are hopping and activation. The effect of doping lithium-iron spinels with impurities of rare earth metals on these conductivity mechanisms was investigated. In work [12], using the generalized Jocher law, the dielectric properties of these spinels were investigated.

The aim of this work is to determine the main parameters of the hopping conductivity and finding their dependence on the content of impurities of rare earth elements La and Y in polycrystalline samples of $Li_2Fe_{2.5-x}Me_xO_4$ (Me = La; Y, x = 0; 0.01; 0.03; 0.05).

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 (≈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

In work [11] temperature dependences of the specific conductivity of synthesized spinels were obtained, which has a semiconducting, activation character and is described by the equation:

$$\sigma = \sigma_\infty \cdot e^{-\frac{\Delta E_a}{2kT}}, \qquad (1)$$

where ΔE_a is the activation energy of the conduction process, k is the Boltzmann constant, σ_∞ is the value of the specific conductivity at $T \to \infty$.

Figure 1 shows the temperature dependences of the specific conductivity for samples of the composition $Li_2Fe_{2,5-x}La_xO_4$ (x = 0; 0,01; 0,03; 0,05). It shows a significant decrease in the specific conductivity of the samples with an increase in the content of lanthanum impurity in them.

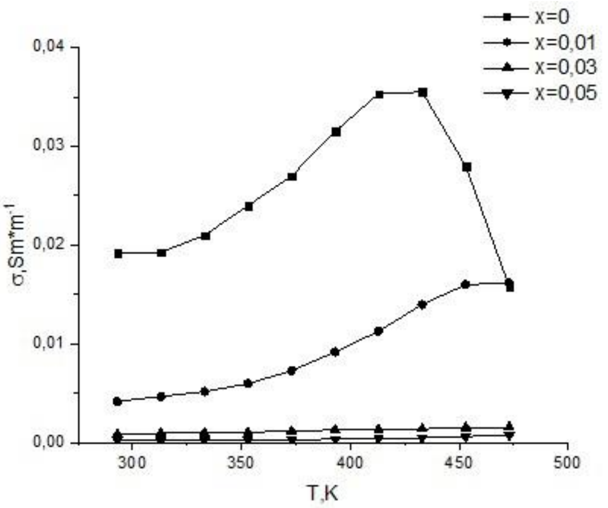

Fig. 1. Experimental temperature dependences of specific conductivity at direct current $Li_{0,5}Fe_{2,5-x}La_xO_4$ spinel for different values of lanthanum content in the samples (x = 0; 0,01; 0,03; 0,05).

In Arrhenius coordinates $ln\sigma(10^3/T)$ (Figure 2), the temperature dependences of conductivity are well approximated by straight lines in the region of high and low temperatures, which is evidence of the manifestation of the activation and hopping mechanism of conductivity, which are characterized by an increase in conductivity with temperature (negative slope of the approximating straight lines). The different slope of the approximating straight lines in these temperature ranges indicates differences in the values of the activation energy of electrical conductivity. In particular, for spinel $Li_{0,5}Fe_{2,5}O_4$ the value of the conductivity activation energy lies within the limits $\Delta E_a = 0{,}04$ eV for the low-temperature region (293-313 K) and $\Delta E_a = 0{,}16$ eV for the high-temperature region (313-433 K). The temperature range above 433 K is characterized by a positive slope of the approximating line, which can be attributed to the manifestation of the metallic type of conductivity. Therefore, in the room temperature region (293-313 K), the dominant conduction mechanism is hopping, the activation energy of which is quite low.

As follows from the results of the analysis of the angles of inclination of the approximating straight lines presented in Figure 2, the presence of a lanthanum impurity leads to an approximately twofold increase in the activation energy of both the hopping (from 0.04 eV to 0.08-0.1 eV) and activation (from 0.16 eV to 0.29-0.31 eV) mechanisms compared to the case of pure (without impurity) lithium-iron spinel. At the same time, with increasing impurity content, the temperature at which the hopping mechanism is replaced by the activation mechanism increases.

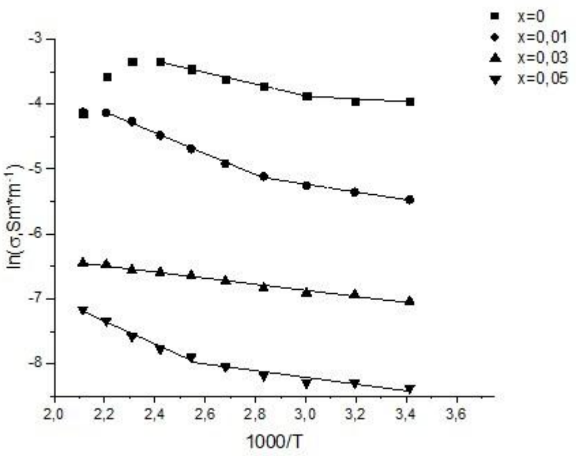

Fig. 2. Experimental Arrhenius curves with selected straight sections for $Li_{0,5}Fe_{2,5-x}La_xO_4$ spinel samples with different lanthanum content in the samples (x = 0; 0,01; 0,03; 0,05).

The hopping mechanism of electrical conductivity in ferrites is mainly realized by electron hopping between ions of the same element, which can be in more than one valence state, randomly distributed in crystallographically equivalent lattice positions [13].

To determine the parameters characterizing the hopping mechanism of conduction, we will apply Mott theory [14]. The dependence of the specific conductivity on temperature in Mott coordinates $\left(ln\sigma T^{\frac{1}{2}}\left(T^{-\frac{1}{4}}\right)\right)$ is also well described by a straight line (Figure 3). In this case, for the specific conductivity according to [15], we can use the expression:

$$\sigma = \frac{\sigma_0}{T^{\frac{1}{2}}} exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{4}}\right]. \tag{2}$$

Here the parameter T_0 is determined by the formula

$$T_0 = \frac{18\left(\frac{1}{a}\right)^3}{kN(E_F)}, \tag{3}$$

the coefficient σ_0 means specific conductivity at the inverse temperature $\frac{1}{T^{1/2}}$, which tends to zero and is found from the expression

$$\sigma_0 = e^2 a^2 \nu_{fn} N(E_F), \tag{4}$$

where e is the electron charge, a is the charge carrier localization radius, ν_{fn} is the lattice vibration frequency, $N(E_F)$ is the density of states near the Fermi level.

To determine the parameters σ_0 and T_0, we use the approximation of the experimental temperature dependences by linear functions $ln\sigma T^{\frac{1}{2}}\left(T^{-\frac{1}{4}}\right)$ (see Figure 3).

The fulfillment of these dependences in the low-temperature region indicates that charge transfer in the studied systems occurs by hopping conduction of electrons over localized states lying in a narrow energy band near the Fermi level. In spinel ferrites, such states are created by the presence in equivalent crystallographic lattice positions of ions of the same element with a valence that differs by one [13] (in this case, these are the ions Fe^{2+} and Fe^{3+}). The corresponding valence states migrate over the crystal, and at a sufficiently high concentration of ions with variable valence, the electrical conductivity has a high value and is characterized by a low activation energy.

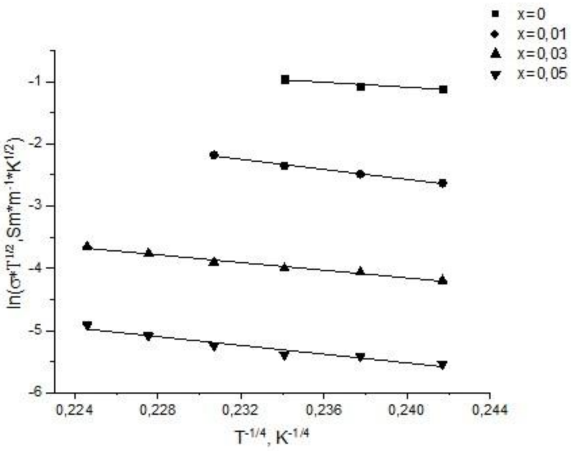

Fig. 3. Straight-line plots of experimental temperature dependences of specific conductivity in Mott coordi-nates for $Li_{0,5}Fe_{2,5-x}La_xO_4$ spinel with different lanthanum contents in the samples (x = 0; 0.01; 0.03; 0.05).

Within the framework of the hopping mechanism of conduction model [15], the average charge carrier hopping length for a given temperature is found from the expression:

$$R = \frac{3}{8} a \left(\frac{T_0}{T}\right)^{\frac{1}{4}} \tag{5}$$

As can be seen from equation (5), the value of the parameter R increases with decreasing temperature. Thereat there is a rapid depletion of local states in the band gap, and hoppings of charge carriers over individual impurity levels without activation into the conduction band begin to play a significant role in the electrical conductivity process. As a result, the probability of charge carrier hoppings to spatially more distant, but energetically closer localization centers (ions Fe^{2+} and Fe^{3+}) increases, which is the reason for the decrease in the activation energy of the hopping.

The magnitude of the energy spread of local states in this case is determined by the formula:

$$\Delta E = \frac{3}{2\pi R^3 N(E_F)} \tag{6}$$

In this case, the concentration of capture centers is found from the relationship:

$$N_t = N(E_F)\Delta E \tag{7}$$

The values of the parameters characterizing the process of hopping charge transfer in lanthanum-doped lithium-iron spinels are presented in Table 1.

Table 1.

The values of the parameters characterizing the process of hopping charge transfer in lanthanum-doped lithium-iron spinels

Ion content La^{+3}, x	Activation energy ΔE_a, eV	$T_0 \cdot 10^5$, K	$N(E_F) \cdot 10^{24}$, eV^{-1}m^{-3}	Hopping length R, $\dot{A}$ at T=293 K	ΔE, eV	$N_t \cdot 10^{24}$, m^{-3}
0.00	0.04	1.6	7.3	74.8	0.16	1.2
0.01	0.10	25.6	375.3	15.9	0.32	118.1
0.03	0.08	9.2	31.0	37.5	0.24	9.1
0.05	0.09	15.4	38.2	38.2	0.28	8.6

For pure lithium-iron spinel, there is a fairly close match between the electron hopping length R and the average distance between divalent and trivalent iron ions d [16]. This coincidence confirms the fact that the hopping is carried out by electron exchange between equivalent differently valent ions. When doping spinel with lanthanum and increasing its content, the average distance d between the iron ions with different valence increases, and as can be seen from Table 1, the electron hopping length R, on the contrary, decreases, especially for the sample with x=0.01. Such a sharp violation of the correlation between R and d indicates that doping lithium-iron spinel with lanthanum leads to the destruction of its hopping conductivity.

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}. The presence of an yttri-um 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, performed in [12], shows that already with the content of yttrium impuriy 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.

Conclusions

In this work, based on the impedance method of research, the hopping mechanism of conductivity of lithium-iron spinels doped with rare earth metals has been analyzed. It is shown that in the temperature dependence of conductivity, three regions can be distinguished, two of which have semiconductor conductivity, but have different activation energy values. The high-temperature region is associated with the activation mechanism of conduction, and the low-temperature region is associated with the hopping mechanism. The main parameters of the hopping conductivity were calculated: the density of states near the Fermi level, the electron hopping length, and the concentration of charge carrier capture centers depending on the lanthanum ion content. It has been shown that under the influence of rare earth metal impurities, the hopping mechanism is destroyed and replaced by an activation one.

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Стрибкова провідність в літій-залізної шпінелі, легованої La,Y

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Методом імпедансної спектроскопії отримані температурно-частотні залежності електричних характеристик $Li_2Fe_{2,5-x}Me_xO_4$ (Me = La; Y, x = 0; 0,01; 0,03; 0,05) шпінелей, синтезованих за технологією «золь-гель» автоспалювання, в інтервалі температур 293-473К. На основі їх аналізу виявлені основні механізми провідності цих матеріалів в досліджуваному інтервалі температур: стрибковий та активаційний. Показано, що при низьких температурах домінує стрибковий механізм провідності. Встановлено основні параметри стрибкової провідності. Досліджено вплив на них легування літій-залізних шпінелей доміщками рідкісноземельних металів.

Ключові слова: імпедансна спектроскопія, шпінель, енергія активації, криві Арреніуса, стрибковий механізм провідності, теорія Мотта.