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INVESTIGATION OF THE INFLUENCE OF RARE-EARTH METAL IMPURITIES ON THE CONDUCTIVITY OF LITHIUM-IRON SPINEL

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Abstract. *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» auto-combustion technology were obtained by the method of impedance spectroscopy in the temperature range of 293-473K. Based on their analysis, the main mechanisms of conductivity of these materials in the studied temperature range were identified: hopping and activation. 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.*

Key words: *impedance spectroscopy, spinel, activation energy, hopping mechanism of conductivity, rare earth elements.*

Introduction.

Spinel ferrites, due to their dielectric and magnetic properties, are widely used in radio-electronic devices of various technical purposes. At the same time, the ability of such materials to intercalate-deintercalate lithium ions into their structure allows them to be considered as a promising material for the manufacture of the cathode matrix 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].

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 [3-5] 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.

Main text.

Atoms and ions of rare earth elements, with a constant valence of +3, have uncompensated spin moments in *f*-orbitals [6]. 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 $5s^2 5p^6$ 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.

In work [7] an investigation was conducted of the temperature-dependent frequency dispersion of the conductive and dielectric properties of lithium-iron spinels doped with two representatives of rare earth metals – lanthanum and yttrium, synthesized using the «sol-gel» autocombustion technology.

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 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.

Analysis of the temperature dependences of direct current conductivity indicates the dominance of electronic conductivity in these ceramics in the temperature range of 293-473 K.

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

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. 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.

Summary and conclusions.

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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