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ELECTRIC PROPERTIES OF Mg-SUBSTITUTED LITHIUM IRON SPINEL

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Abstract: Complex impedances of sintered polycrystalline $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ (x = 0.0, 0.1, 0.3, 0.6, 0.8, 1.0) ferrite in the frequency range of 0.01 Hz to 100 kHz were measured at several temperatures in the range of 295-723 K. The complex-plane impedance spectra indicate that the material can be represented by a two-layer leaky capacitor which corresponds to the bulk and the grain boundary phenomena at high and low frequencies respectively. The dependence of impedance and conductivity and dielectric properties on temperature and frequency are discussed.

Keywords: ferrite, complex impedance, dielectric constant, dielectric losses, polarization.

1. INTRODUCTION

Lithium ferrites are of considerable interest owing to their acceptable dielectric properties which depend on a number of factors: a method of preparation [8], temperature [7, 14], atmosphere of sintering [7, 8], as well as iso- and heterovalent substitution [2]. The structure of a spinel being crystal, it allows to carry out substitution in a fairly wide range, while remaining one phase. Especially interesting in this case are ions of magnesium. With a slight advantage over the oxygen octaenvironment in the spinel structure ions of magnesium can move in both sub lattices replacing iron practically in a stoichiometric ratio [3]. In their electric properties ferretes belong to the class called valency-controlled semiconductors. This is a group of transition metals oxides with a blank 3d - shell, so they are under certain conditions [11] may obtain a metallic type of conductivity. However, samples of stoichiometric composition in the absence of additives are dielectrics. Conductivity of these oxides can be increased by introducing in the lattice additives of other elements [11]. Low resistance, due to the simultaneous presence of two- and trivalency ions of iron in the equivalent nodes of stoichiometric oxides lattice, can also be achieved by a valency - controlled method. If a small amount of extraneous ions, valence of which differs from the valency of stoichiometric composition, is introduced in the oxide with a high resistance, then a part of ions changes its valence. As a result, ions of the same atom have different valence, and electrical resistance of oxide falls [4].

In order to find out the impact of substitution on the dielectric properties of *Mg*-doped lithium iron spinels, we have by method of complex electric impedance conducted a systematic research of dielectric constants and losses of tangent as a function of composition and the frequency both at room temperature and in a wide temperature range.

2. EXPERIMENTAL PROCEDURE

Synthesis of the general stoichiometric composition $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ (x = 0.0, 0.1, 0.3, 0.6, 0.8, 1.0) was a standard ceramic technology of double sintering with outgoing oxides Fe_2O_3, MgO and lithium hydroxide $LiON$ grade. An X-ray study of synthesized compounds on the diffractometer DRON-3 in $CuK\alpha$- radiation showed the samples obtained as single-phase and their belonging to the spatial group Fd3m, cation distribution was found by Ritveld' method. Based on cationic distribution of magnesium and iron ions as well as on the terms of electroneutrality it was discovered that lithium ions were both in octa- and tetra positions [3]. In this same work the results of x-ray studies were confirmed by the method of messbauer spectroscopy.

Coinductivity of alternating current, the tangent of losses, the real and imaginary parts of penetration were determined on the basis of experimental dependencies of complex impedance, obtained at the spectrometer $Autolab\ PGSTAT\ 12/FRA-2$ in the frequency range 0.01Hz-100 kHz. The temperature dependence obtained was based on the impedance studies in step-by-step mode heating with isothermal exposure after every 50 degrees in the temperature range 295-723 K. Frequency dependence of dielectric functions was derived from the experimental Nyquist 's diagram (Fig. 2, b):

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

$$M^* = M' + jM''$$

$$Z^* = Z' - jZ''$$

$$Y^* = Y' + jY''$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

$$\varepsilon^* = j\omega C_0 Y^*$$

where ε^* - complex dielectric permeability, M^*- complex coefficient (module), Z^* - complex impedance, Y^*- comprehensive admittance, ω - cyclic frequency, j - imaginary unit, C_0 - capacity of the system.

3. RESULTS AND DISCUSSION

The change of the specific resistance to direct current ρ_{dc} and dielectric constant ε' depending on the content of magnesium ions are shown in Fig. 1. As it can be seen from the Figure, ρ_{dc} and ε' are mutually inverse dependent. This tendency is quite understandable, since the basis of activity of conductivity and polarization of ferrite systems are one and the same processes; and it is a jump of an electron $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$ that results in a local bias charge and holds responsible for polarization. The presence of Fe^{2+} in the octahedral cavities of iron spinels is decisive for implementation of the intermittent mechanism of conductivity and depends on the conditions of synthesis: time of sintering[8], temperature [14], the speed of cooling [14, 3], etc. With increasing the content of Mg^{2+} ions is natural, and it decreases the concentration of Fe^{2+} ions [14], however, as is seen from Fig. 1, resistivity weakly depends on the content of magnesium ions in $x \geq 0.1$. The following behavior can be clearly explained by the fact that the presence of lithium ions in the octasublattice leads to the formation of complexes of the type $[Li^+ + Fe^{3+}]$ that in general behave like Fe^{2+} and capable to take a ' wandering' electron, and so get involved in the intermittent mechanism of conductivity. The frequency of electronic navigation $Fe^{3+} + e \leftrightarrow Fe^{2+}$ depends on the structure of ferrites, concentration of defects, loosely-tied electrons, and temperature of ferrites. Transitions $Fe^{3+} + e \leftrightarrow Fe^{2+}$ occur between Fe ions in the octahedral cavities, as in small tetrahedral intervals iron ions can be found mainly in the three-valency state. Loosely-tied electrons are responsible for the semiconductor properties of ferrite and determine its main electrical properties.

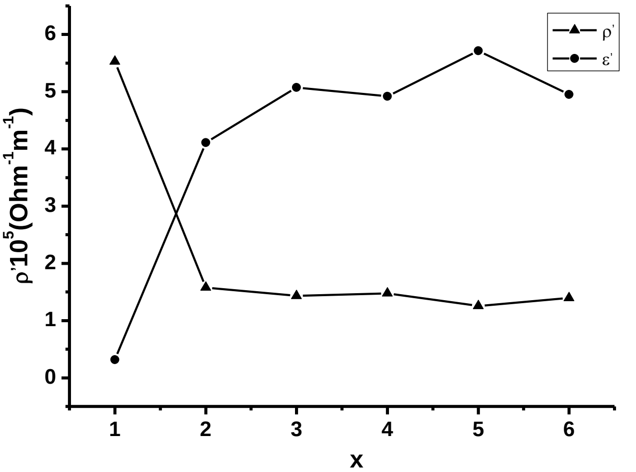


Fig. 1. Dependence of dielectric permeability and conductivity on the direct current from the samples of $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ *(x = 0.0, 0.1, 0.3, 0.6, 0.8, 1.0)*

In Fig. 2 is frequency dependence of conductivity of the sample composition of $Li_{0.5}Fe_{2.4}Mg_{0.1}O_4$ at different temperatures. At relatively low temperatures conductivity defects dependency on frequency, however, ranging from temperature 573K such dependence disappears , indicating the metal-type of conductivity. Frequency dispersion of conductivity at low temperatures is often associated with determining influence [6] inter crystalline transitions.

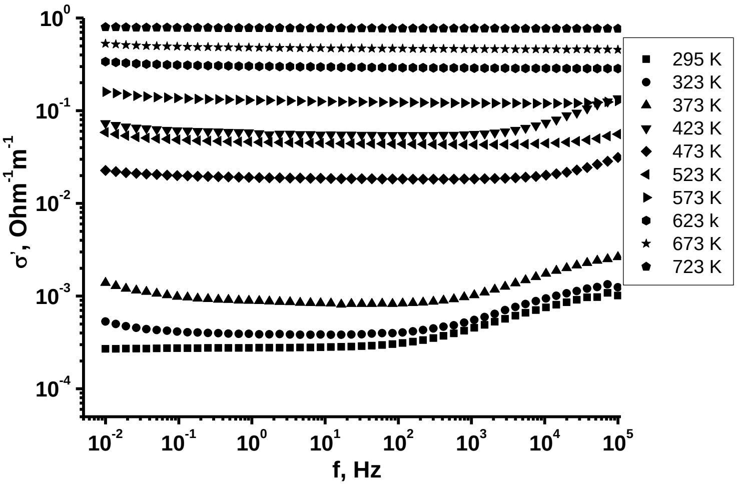
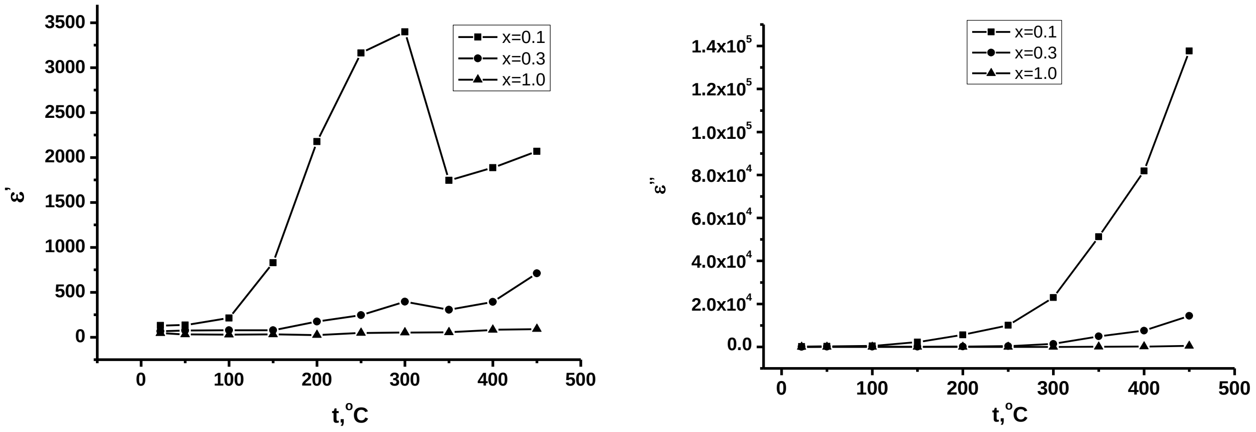


Fig. 2. Dependence of the real part of conductivity on frequency of the system of $Li_{0.5}Fe_{2.4}Mg_{0.1}O_4$

This change of electrophysical settings can be explained within a model of heterogeneous leading environment [10], which is polycrystalline ferrites. According to this model, the strata of varying conductivity occur both on the framework of grains and other inhomogeneities, such as i.e.,domains, dislocations, etc. On the framework emerge locking layers from different sides of such heterogeneities, and locking layers are oriented in straight and locking directions at a certain polarity of the external field. In the works [1, 10] it is concluded that the growth of conductivity with temperature and frequency in polycrystals are due to the effect of tunneling electrons through the inter grain layer. Thus, electrophysical parameters are largely determined by the microstructure of samples.

In Fig. 3 temperature dependences of real and imaginary parts of dielectric permeability of samples. $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ (x = 0.1, 0.3, 1.0).



(a) *(b)*

Fig. 3. Temperature dependence of real (a) and imaginary (b) part of dielectric permeability of samples $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ *(x = 0.1, 0.3, 1.0)*

Temperature dependencies ε'' are described by smooth curves , the progress of which has a different character in low and high temperatures. With increasing temperature above T=400K, the imaginary part of dielectric permeability grows stronger with decreasing content of *Mg* ions. Temperature dependences of the real part of dielectric permeability are characterized by the presence of the peak which is most strongly manifested by the sample composition $Li_{0.5}Fe_{2.4}Mg_{0.1}O_4$. With increasing content of *Mg* ions its position shifts in high temperature and is accompanied by a decrease in intensity. For the sample with the greatest concentration Mg^{2+} this peak is missing, and weak dependence of the real part of dielectric permeability can be observed. Dependencies of σ and ε on frequency f and temperature *T* for polycrystalline ferrites [5] are made to interpret within a model of interlayer polarization and interlayer polarization with the participation of external condition of inter grain framework. One of the main reasons for the emergence of interlayer polarization is the process of electrical transfer. Obviously, a certain temperature (in this case 475-575 K) activates electronic transitions between the ions of variable valence ($Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$) and such a recharge of ion pairs is the process of dipole reorientation in an alternating field. We can assume that the growth of ε' is due to polarization or (it is more probable) a recharge of pairs in the electrical domains formed spontaneously at this temperature under the influence of the applied electric field. Preceding from this assumption we can suggest that with increasing temperature of the sample these domains are destroyed as a result of the growth of thermal motion of ions, and, as it can be seen from Fig. 2, b, causing the reduction of dielectric permeability. A slight growth of $\varepsilon'(T)$ at temperatures above 625 K is apparently caused by individual recharge of iron ions of different valency. This phenomenon is observed in the works [9, 13], which make assumptions about the manifestation of the effect of ferroelectrics.

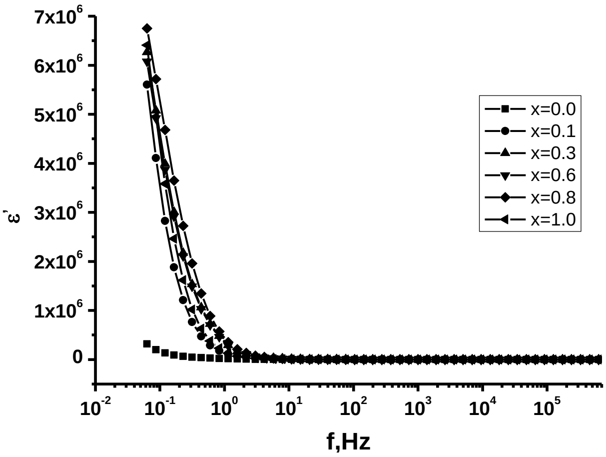


Fig. 4. Dependence of the real part of dielectric permeability on frequency

Frequency and temperature characteristics of dielectric permeability of ferrites to a great extent depend on their composition and structure. At room temperature and frequency of 0.01 Hz the value of ε' is a value of 10^6 order for all compositions, with increasing frequency comes the reduction of value ε' and makes up 10-20 at high frequencies. Dipoles that are formed under the influence of an alternating electric field by electrons and ionic vacancies are obviously the main reason for high dielectric permeability of samples. However, other processes can contribute to the value of this magnitude, the processes that take place in ferrites, in particular, those that are related to the heterogeneity of these systems.

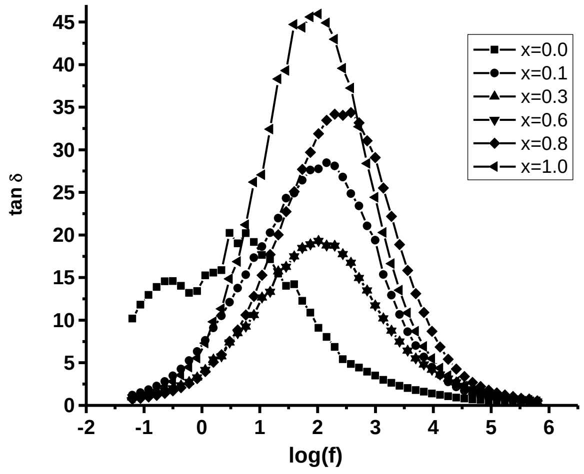


Fig. 5. Dependence of dielectric tangent of losses ($tg\delta$) on the frequency in the samples of $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ *(x = 0.0, 0.1, 0.3, 0.6, 0.8, 1.0)*

In an alternating electric field all processes of displacement and orientation of ferrite particles will have a place until the time these processes are smaller than a half period of changes in an external electric field. The important characteristic is the time of relaxation τ that determines the orientation of the dipole in an alternating electric field. In connection with the late relaxative polarization the energy is dissipated and heats up on the alternating current. The power dissipated in the unit of volume is characterized by a tangent of angle of dielectric losses *($tg\delta$)*. In Fig. 5 is a frequency dependence of dielectric tangent of losses, in which you can see that the height and shape of the curve depend on the composition and microstructure of samples. For x=0.0 there are two distinctly separated peaks at frequencies 10^{-1} and 10 Hz which usually contribute to the polarization of grains and their framework. Significant expansion of the curve for other samples suggests the presence of two kinds of contribution to polarization that occur at two similar frequencies. The average value of relaxation time for samples of Mg - substituted lithium-iron spinel $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ (x = 0.0, 0.1, 0.3, 0.6, 0.8, 1.0), obtained from experimental dependencies of tangent of dielectric losses on frequency, is from 0.014 (for x=0.8) to 0.047 (for x=1.0). Dependence of relaxation time on composition is in Fig. 6.

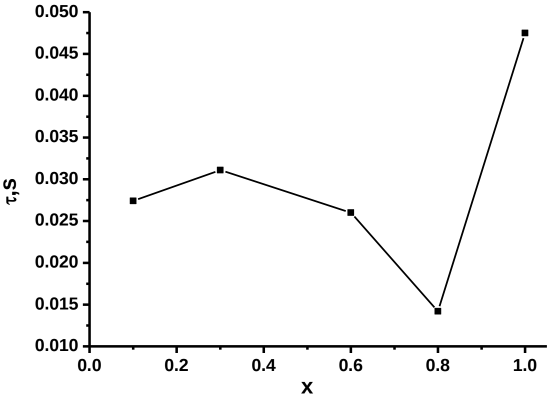


Fig. 6. Dependence of relaxation time of polarization on the content of magnesium ions

Peak expansion of tangent of dielectric losses ($\tan\delta$), as well as the value of relaxation time point out the existence of relaxation time dependence on frequency and not on its constant value [5]. This distribution of relaxation time is a consequence of the difference in the inner circle of different ions in the structure under study, besides, of influence are temperature fluctuations of the lattice at room temperature.

4. CONCLUSION

An impedance range-based analysis shows that behavior of temperature dependence of the real part of dielectric permeability is characterized by the presence of the maximum in the temperature range of 475-575 K that is evidently connected with the processes of activating electronic transfers between ions of variable valence , and is accompanied by dipole reorganization in the AC field. A characteristic view of frequency dependence σ' testifies to the presence in a Mg-substituted lithium – iron spinel $Li_{0.5}Fe_{2.4}Mg_{0.1}O_4$ dc – electric conductivity, the contribution of which increases with temperature, and at T> 573 K its share in conductivity gets predominant.

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Кайкан Л.С., Гасюк І.М., Угорчук В.В., Кайкан Ю.С., Січка М.Я. Електричні властивості магній – заміщеної літій – залізної шпінелі. *Журнал Прикарпатського університету імені Василя Стефаника*, **1** (1) (2014), 9–15.

Полікристалічні ферити $Li_{0.5}Fe_{2.5-x}Mg_xO_4$ (x = 0.0, 0.1, 0.3, 0.6, 0.8, 1.0) досліджувались методом комплексного імпедансу в частотному діапазоні від 0,01 Гц до 100 кГц при різних температурах в околі 295-723 К. Спектри комплексного імпедансу показали, що досліджуваний матеріал може бути представлений у вигляді двошарового конденсатора, властивості яких відповідають за зерна і границі зерен матеріалу при високих і низьких частотах. Обговорюються температурні залежності провідності та діелектричної проникності.

Ключові слова: ферити, комплексний імпеданс, діелектрична проникність, діелектричні втрати, поляризація.