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TEMPERATURE FREQUENCY CHARACTERISTICS OF CHARGE TRANSITION IN THE $Li_{0.5}Fe_{2.4}Ti_{0.1}O_4$ NON-STOICHIOMETRIC SYSTEM

I.M. GASYUK, V.V. UGORCHUK, L.S. KAYKAN, B.J. DEPUTAT

Abstract: A study of conductivity temperature frequency dependence of $Li_{0.5}Fe_{2.4}Ti_{0.1}O_4$ non-stoichiometric spinel has exhibited frequency dispersion conductivity presence. The time of relaxation (τ) proved to make $2\cdot10^{-6}$s within the limits of dispersion. The conductivity size was found to be dependant upon the amount of Fe^{2+} ions in the structure.

Keywords: spinel, energy of activation, Koops' model, conductivity.

1. INTRODUCTION

Stoichiometric lithium ferrospinel $Li_{0.5}Fe_{2.5}O_4$ was studied as a long-range composition of the magnetoactive systems.

These chemical agents possess the rectangular hysteresis loop and the specific phase transformation at the Koori point [2, 7, 8] that allows them to be used in a data storing device. The progress in the digital recording and electronic devices downsizing made the lithium ferric ferrite, the so-called solids, unpopular for research. The special features of a crystalline composition like spinel, natural for these systems, are particularly available through a crystallographic vacancy. This allows us to use them in prospect with a level of other spinels as the cathode active composition of the electrochemical sources of current with the lithium anode. The micro measured crystallites' intercalative characteristics are like popular nanoporous and tabular systems as TiO_2, CoO_2, $GaAs$ etc. [3, 12].

Nevertheless, the cathode formation technology provides for the electro conductive additive like graphite, carbon, or any other conductor. Concentration of this component increases in case of crystal grains, which reduces the operating characteristics of lithium current sources.

The problem can be solved in different ways, one of which is spinel synthesis modification in the forming stage of composition by adding different valency ions to the structure [15]. Not only does this method help to change the electronic or p-type conductivity in the composition, it also provides it with specific dielectric properties.

Thus, fair quantity of the modified lithium containing spinels has ion conductivity that lets use them as the solid state electrolyte in the high-temperature current sources [1, 6, 20]. In both cases of spinel alloys' practical application one of the determinative manageable indicators are the conductive and dielectric properties of the composition. They stipulate both electronic spectrum and crystalline structure which is formed in the process of synthesis, and microstructure determined by polycrystalline grain composition characteristics and intergrain interface [1, 21]. Synthesis adding of metal ions is one of the primary methods of influencing the oxide spinel physical chemical characteristics.

This work has focused on investigation of changing physical properties and spinel *Li-Fe* structure by way of adding univalent, bivalent, trivalent and tetravalent ions. However, analysis of related literature showed that there are no integrated studies in the lithium ferrospinel electroconductive and dielectric characteristics, added with Ti ions, yet the very systems are rather valuable for the lithium source of current in the cathode system aspect [14]. The study [10] presents only the low-frequency dielectric ferrites' qualities of $Li_{0.5+0.5a}Fe_{2.5-1.5a}Ti_aO_4$ $(a = 0,\ 0.1,\ 0.2,\ ...0.7)$ composition and analysis of infrared spectra of substance absorption. Frequency temperature dependence of conducting properties of a $Li_{0.5}Fe_{2.4}Ti_{0.1}O_4$ non-stoichiometric system composition has been studied by the method of complex impedance. This composition in regarded to be a long-range active material of the lithium current source cathodes for wide use [18].

2. EXPERIMENTAL PROCEDURE

Polycrystalline samples were obtained according to the traditional ceramic method [23] from Fe_2O_3, TiO_2 (rutile) powder and $LiOH$. Complete synthesis was done by the air sintering method at 1473 K temperature for 8 hours and slow cooling together with a kiln. The process details are described in work [15]. Impedance locus $Z' = f(Z'')$, where Z', Z'' – real and ideal parts of the system complex resistance ($Z = Z' - jZ''$, j – ideal unity) was obtained with the help of impedance spectrometer Autolab PGSTAT 12/FRA- 2 in frequency range 0.01–10^5Hz. The electroconductive dope, which had been applied on the flat perform – sample, was used as an electrode. Under these conditions the ion conductance formed a block and the charge was transferred by the electrons. The sinusoidal voltage amplitude amounted 100mV. The temperature was measured from room temperature to 673 K in increments of 50 K with the help of the SNOL 7.2/1100 kiln that provides temperature control and measurement ~1K.

3. RESULTS AND DISCUSSION

The impedance spectra of the $Li_{0.5}Fe_{2.4}Ti_{0.1}O_4$ system are shown in Fig. 1 in the Nyquist coordinates for different temperatures.

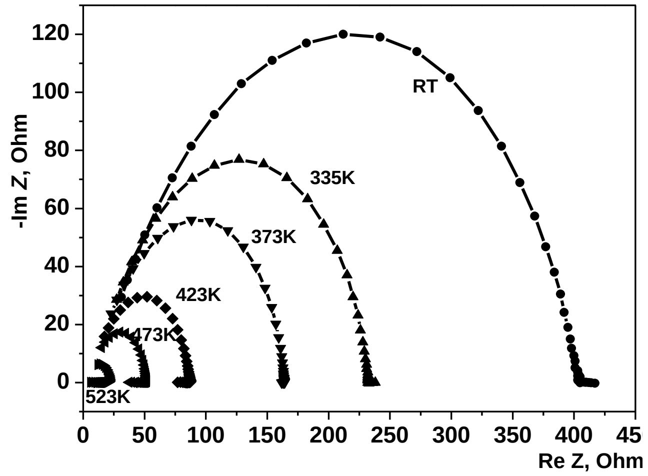

Fig. 1. Impedance temperature dependence locus diagram for $Li_{0,5}Fe_{2.4}Ti_{0.1}O_4$ *system*

The parametric dependence diagrams $Z' = f(Z'')$, where Z', Z'' – are frequency functions and have an arch shape for all temperature limits of the sample composition under research.

One of the main criteria for the electroconductivity measuring technique is its external electric field frequency dependence. In case of the intermittent mechanism the conductivity increases compared to zone conductivity, which does not depend upon the external field frequency up to $f = 10^9 \ldots 10^{11}$ *Hz* frequency [4, 19].

Frequency dependence of the specific conductivity $\sigma(f)$ (AC – conductivity) for different temperatures is shown in Fig. 2. The $\sigma(f)$ level weakly depends upon the frequency in the $f = 0.01 - 10^3$ *Hz* range. Increasing f upwards of 10^3 Hz abrupt growth of conductivity up to the researched frequency range is observed. At a lower temperature σ dependence is more expressed.

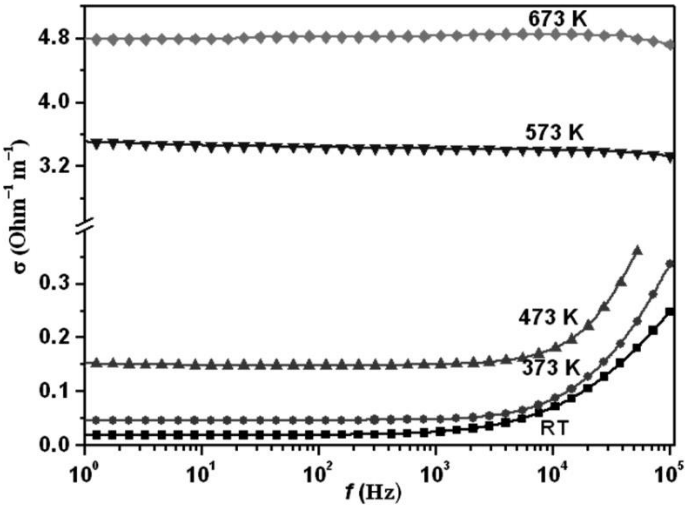

Fig. 2. Frequency and temperature σ dependence graphic chart

In the ferrite physics the most known sample part, first examined in the works of Wagner, Koops etc. [5, 10, 11, 17], can exemplify the obtained results of the AC frequency dependent conductivity. According to that sample part, the spinel is the molded multilayer condenser, grains and grain boundaries of which have different conducting properties. The polycrystalline spinel is supposed to contain large, comparatively high conductivity range with the resistivity constant ρ_g and dielectric penetration ε_g, which are divided with the thin layers of comparatively low conductivity substance with the ρ_b and ε_b amount, that is low-resistance grains and high-resistance grain boundaries. The impedance of such sample part can be shown by the equivalent electric circuit (Fig. 3), where R_1, C_1 and R_2, C_2 are respectively active resistance and capacity reactance of the grains and grain boundaries. The conductivity growth at frequency becomes clear in consideration of the fact that the high-resistance polycrystalline intergrain boundaries "bridging" takes place on the ac field at a certain signal frequency [9].

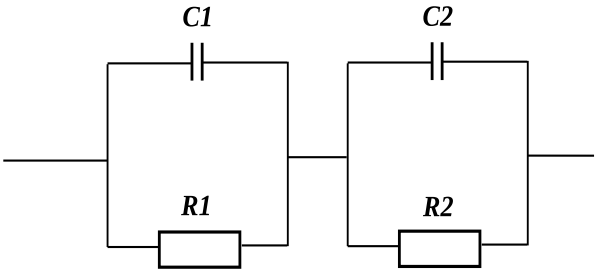

Fig. 3. Equivalent circuit of the grain – layer segment

In the high-frequency range the capacity reactance gets less than active resistance. As a result the whole polycrystalline conductivity is rated by the grains properties whereas the intergrain potential barrier influence at the "grain – boundary" range can be neglected. The distinctive feature of such an effect is the increasing amount of the spinel specific conductivity σ and the decreasing of electrical transit activation energy at the electric field frequency growth. The frequency dispersion σ can be described with the help of the relaxation composition [10, 22],

$$\sigma(f)=\sigma_{lf}+\frac{\sigma_{lf}-\sigma_{hf}}{1+(2\pi f\tau)^2} \tag{1}$$

where *lf* and *hf* indicate the limitation level at low (approximately 10^3 Hz) and high (approximately 10^5 Hz), respectively. Relaxation time τ is the qualitative scratch constant for spinels and it has been calculated according to the equation (1). Magnitude τ was revealed to be within the limit (2-6)·10^{-6}s. The generic magnitude τ has been used for approaching the curves $\sigma(f)$, the trends of which coordinate with the experiment (Fig. 4).

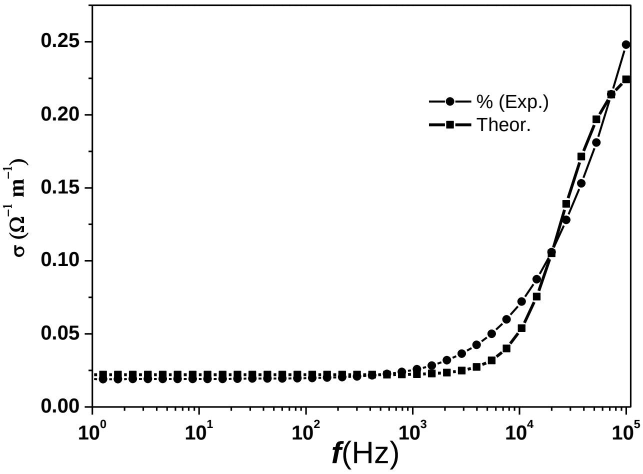

Fig. 4. Experimental and theoretical AC conductivity dependence upon frequency

The electric conductivity mode of behaviour can be explained by the electronic overshooting model $Fe^{2+} \to Fe^{3+} + e^-$, realized by the electron exchange among certain octahedral positions (B-positions) in the spinel grate [16]. It means that frequency in the range of $10^3 – 10^5$ Hz, fits the electronic overshooting frequency, and influences the electron exchange as far as the frequencies less than 10^3 Hz. The external field does not facilitate the exchange technique. The mode of conductivity behaviour at high frequency of applied electric field $f > 5\cdot10^2$ Hz results from electron exchange among Fe^{2+} i Fe^{3+} and does not depend upon this frequency.

Let us consider temperature – frequency dependence of the substance conductivity in question (Fig. 5).

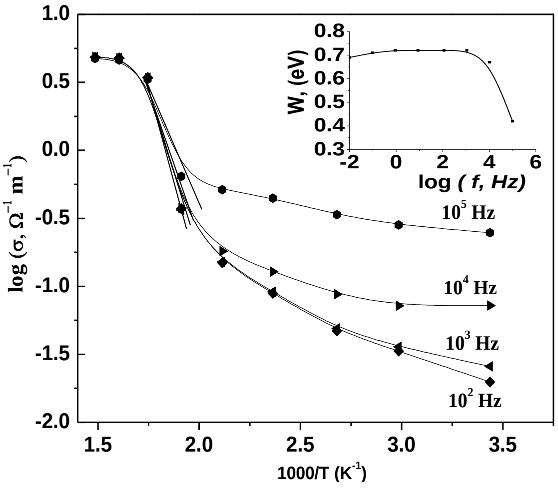

***Fig. 5.** Dependence of log σ as function of T^{-1} at different frequencies*

Whereas the spinel oxide is considered to be the semiconductors with the low charge carrier mobility, conductivity dependence upon temperature as a rule is of semiconducting nature and can be expressed by:

$$\sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right) \tag{2}$$

where σ_0 is a pre-exponent multiplier, which does not depend upon temperature and possesses the semiconductor properties, W is activation conductivity energy, T is absolute temperature, k is Boltzmann constant.

The dominant factor in the conductivity process is the charge carrier mobility. Its influence increases at the temperature according to the exponential law and can be determined by the thermal activation energy of W order that exceeds the overshooting potential barrier activation between two B-positions. The barrier negotiation at grain boundary is also obvious. On dependence σ (T^{-1}), modified in Arrhenius coordinates for different frequencies at temperature ~ 500 K, the faintly expressed hump is retraced. It denotes the conversion from the semiconducting nature of conductivity to the metallic one [24].

The conductivity activation energy magnitude W, was calculated for the rectilinear range (intrinsic zone [17] log $\sigma(T^{-1})$ dependence) at a high magnitude of temperature T (about 420 K) graphic of fig. 5. Magnitude W tends toward decreasing in frequency increasing and increases at the Fe^{2+} ion number reduction. Obviously, it can be explained by the exaggeration of the overshooting electron flow conditions.

4. CONCLUSIONS

1. For the first time for non-stoichiometric $Li_{0.5}Fe_{2.4}Ti_{0.1}O_4$ spinel, the temperature frequency dependence of the specific conductance has been fixed while studying the impedance spectra locus curves in the frequency range of 0.01 – 10^5 Hz and temperature range from room to 673 K.

2. Using the classical Debby formulae for the stereotyped dipoles, the specific conductivity experimental dependence upon the external electric field at non-stoichiometric composition sample has been approximated. The qualitative time of the relaxation charging has been inserted to be within (2-6) $\cdot 10^{-6}$ s and is not dependant upon the sample composition and temperature.

3. By measuring the results of spinel conductivity, dependence of electric conductivity activation energy upon the applied electric field frequency has been set. The conductivity activation energy level is determined to decrease with the applied external electric field increase and is rated by the Fe^{2+} ions concentration at the spinel phase of the sample.

4. At temperatures of 500 K the system under study changes the conductivity nature from semiconducting to metallic.

5. The non-stoichiometric spinel of $Li_{0.5}Fe_{2.4}Ti_{0.1}O_4$ composition, obtained by the ceramic method, possesses high conductivity that makes it a prospective cathode system for electrochemical lithium source of current.

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Address: I.M. Gasyuk, V.V. Ugorchuk, L.S. Kaykan, B.J. Deputat: Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano- Frankivsk, 76025, Ukraine.

E-mail: gasyukim@pu.if.ua**;** uhorchuk@rambler.ru.

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Гасюк І.М., Угорчук В.В., Кайкан Л.С., Депутат В.Ю. Температурно-частотні характеристики перенесення заряду у нестехіометричній системі $Li_{0,5}Fe_{2,4}Ti_{0,1}O_4$. *Журнал Прикарпатського університету імені Василя Стефаника*, **1** (1) (2014), 73–79.

Вивчалися температурно-частотні залежності провідності нестехіометричної шпінелі $Li_{0,5}Fe_{2,4}Ti_{0,1}O_4$; виявлено існування частотної дисперсії провідності. У межах дисперсії показано, що час релаксації (τ) становить $2 \cdot 10^{-6}$ с. Експериментально встановлено, що величина провідності залежить від кількості іонів Fe^{2+} у структурі.

Ключові слова: шпінель, енергія активації, модель Вагнера-Купса, провідність.