Electrical properties of lithium ferrite with addition of ZrO_2

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Abstract. The study of electrical properties of composite ceramics based on lithium ferrite $LiFe_5O_8$ with the addition of ZrO_2 (1 and 2 wt%) was carried out. The samples were prepared by standard ceramic technology. Synthesis of lithium ferrite was conducted at 800°C for 120 minutes. The zirconium dioxide was added to synthesized powder by mixing in planetary ball mill, and then the composite powders were sintered at temperatures of 1100°C and 1050ºC. The electrical conductivity of the samples was studied using two-probe spreading resistance method. It was found that addition of ZrO_2 and an increase of its up to 2 wt% leads to increase in the activation energy and electrical resistivity.

1. Introduction

Lithium ferrite ($LiFe_5O_8$) is widespread as the microwave ferrite material. The high Curie temperature (above 600°C) and saturation magnetization (about 3600 G) allowed to create a number of substituted lithium ferrites, which have been used in various microwave and high frequency devices [1-2]. For such ferrite systems, an important parameter is the high electrical resistivity ($\rho > 10^6$ Om·cm) providing low dielectric loss of material. Previously, the preparation of $LiFe_5O_8$ by the standard ceramic technology was studied [3-7]. Also, the dielectric and magnetic properties of these compounds were investigated [1, 2, 8-12].

It was previously demonstrated [13, 14], the small amounts (< 5 wt%) of ZrO_2 may be used as an effective additive in the manufacture of some ferrite materials, which significantly influences on the microstructure and magnetic properties of ferrites. Thus, it was found that the introduction of ZrO_2 into Li-Zn ferrite during synthesis leads to increase the value of initial magnetic permeability of ferrites and reduce the magnetic losses [15]. Moreover, the addition of ZrO2 during high temperature sintering improves the mechanical properties of nickel ferrite, such as a bending strength, microhardness and fracture toughness [16]. It was shown that ZrO2 is insoluble in the ferrites at high temperatures, and the composite materials, such as $ZrO_2/NiFe_2O_4$ in [17], are obtained after sintering.

In this paper, the influence of ZrO_2 addition (1 and 2 wt%) on the electrical conductivity of $LiFe_5O_8$ lithium ferrite was studied.

2. Experimental

Lithium ferrite samples were prepared by standard ceramic technology. Iron oxide (Fe_2O_3) and lithium carbonate (Li_2CO_3) with a ratio of 1:5 were used as the initial reagents to produce lithium ferrite. Before weighing, initial powders were dried for three hours at a temperature of 200ºC in a laboratory furnace. The mixed powder was milled in ball mill during 10 minutes to homogenize the mixture of initial reagents. Synthesis of lithium ferrite was conducted at 800°C for 120 minutes in "HimLabo" standard laboratory oven. The synthesized lithium ferrite powder was divided into several parts. The samples from the first part were sintered at a temperature of 1050ºC for 2 hours (LF_1050). The samples from the second part were sintered for 2 hours at a temperature of 1100ºC (LF_1100).

The zirconium dioxide with 1 and 2 wt% was added to synthesized powder from third and fourth parts by mixing in planetary ball mill. Then, the composite powders were sintered in ceramic samples at temperatures of 1100°C and 1050ºC (LF_1_1050, LF_1_1100 - the lithium ferrites with 1 wt% ZrO_2 were sintered at a temperature of 1050ºC and 1100°C, respectively; LF_2_1050, LF_2_1100 - the lithium ferrites with 2 wt% ZrO_2 were sintered at a temperature of 1050ºC and 1100°C, respectively).

The electrical conductivity of the lithium ceramic was investigated by spreading resistance method [10, 18]. In this case, the electrical resistivity was calculated by the equations:

$$\rho = \frac{U \cdot r_0 \cdot \pi}{I}, \quad (1)$$

where U – applied voltage, I – current intensity, r_0 – contact diameter.

Since the spreading resistance is mainly determined by the contact region, the thickness of which is r_0, the method is characterized by high local measurement. The resolution of the method corresponds to the diameter of the contact, and is ~ 10 µm.

3. Results and discussion

Figures 1 and 2 shows the temperature dependence of the conductivity current for samples sintered at a temperature of 1050ºC (figure 1) and 1100°C (figure 2). It can be seen that the curves for electrical conductivity current versus temperature are characterized by linear dependence in logarithmic coordinates for all lithium ferrite samples. The electrical conductivity of ferrite samples increases with the increasing temperature. A similar character of Ln(I)=f(1/kT) dependencies indicates that the addition of ZrO_2 has not significant effect on the mechanism of electric transport in lithium ferrites, which is determined by electron hopping between Fe^{2+} and Fe^{3+} heterovalent ions [8].

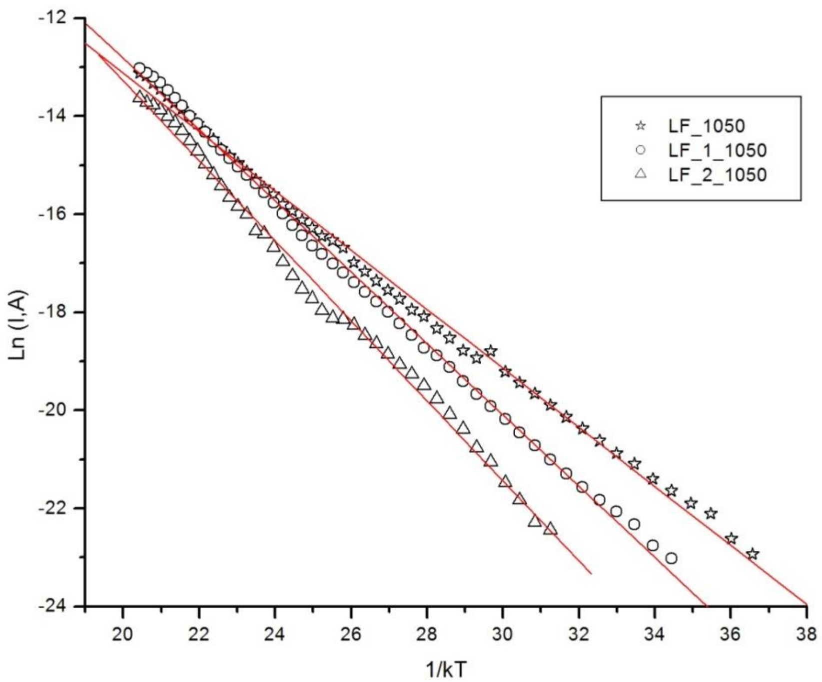

Figure 1. The temperature dependence of conductivity current for samples sintered at 1050ºC.

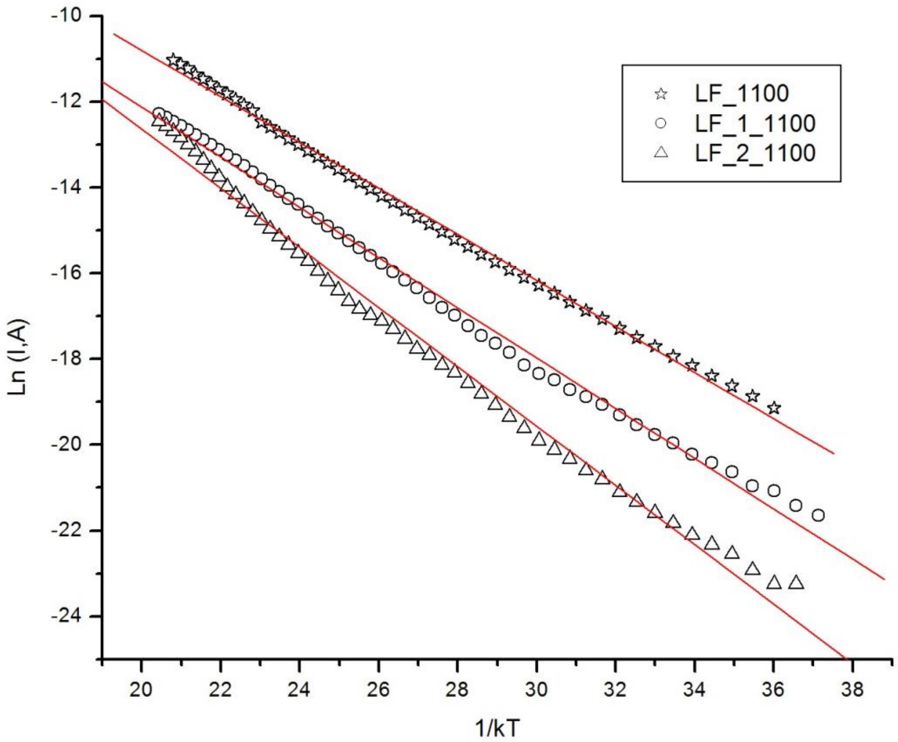

Figure 2. The temperature dependence of conductivity current for samples sintered at 1100ºC.

From electrical conductivity results for all samples, the values of activation energy for electronic conduction (E_a) were found as the tangent of the angle slope of the curves in the temperature dependence of conductivity current. Moreover, the electrical resistivity for all samples was calculated using the equations (1). These electrophysical parameters are shown in table 1. The presented data show that the samples are characterized by the high values of the electrical resistivity, which is typical for lithium ferrite. However, the increase in the sintering temperature for samples, as previously were repeatedly shown [19, 20], reduces the electrical resistance of the samples, which is associated with an increase in the concentration of Fe^{2+} ions.

The results showed that the activation energy and electrical conductivity values increase with increasing the ZrO_2 addition. This can be attributed to changes in the microstructure of ferrite samples.

Table 1. Electrophysical parameters of ferrite samples.

Samples	E_a, (eV)	ρ, (MOm·cm)
LF_1050	0.602	2.61
LF_1_1050	0.726	5.45
LF_2_1050	0.816	16.354
LF_1100	0.536	0.127
LF_1_1100	0.585	0.882
LF_2_1100	0.69	4.015

4. Conclusion

Lithium ferrites with the addition of ZrO_2 have semiconducting properties. The results showed that electrical conductivity increases with increasing temperature, and characterizes by linear dependence.

The electrophysical parameters, such as the activation energy for electronic conduction and electrical resistivity, were found for all samples, and are characterized by the high values typically for lithium ferrites. It was assumed that the conductivity mechanism are unchanged in the temperature range of 20 - 300°C, and is determined by the hopping of electrons between Fe^{2+} и Fe^{3+} ions.

It was found that addition of ZrO_2 and an increase of its up to 2 wt% leads to increase in the activation energy and electrical resistivity. This can be attributed to change in the microstructure of ferrite samples.

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