PHYSICS OF MAGNETIC PHENOMENA

INVESTIGATION OF ELECTROCONDUCTIVITY OF LITHIUM PENTAFERRITE

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Using a double-probe spreading resistance measurement technique combined with a layer-by-layer analysis, temperature dependences of electroconductivity of polycrystalline lithium pentaferrite (LPF), which is produced via a ceramic-production technological process, are investigated. It is shown that the electroconductivity activation energy of LPF is controlled by the height of grain-boundary potential barrier due to different degrees of grain boundary and grain bulk oxidation. A relationship is established between the value of the electroconductivity activation energy of LPF and the processes of its oxygen exchange with the surrounding medium during thermal annealing.

INTRODUCTION

Lithium pentaferrite ($Li_{0,5}Fe_{2,5}O_4$) is the simplest representative of a large class of lithium oxide ferrospinels exhibiting a wide variety of compositions and structure modifications. It is, therefore, an attractive candidate primarily as a model object in investigating fundamental physical phenomena taking place in materials based on LPF. It was particularly challenging, using this material as a model object, to obtain useful information on characteristic features and efficiency of redox reactions under different conditions of thermal treatment of LPF.

From among the approaches available, the technique of electroconductivity measurement reported in [1] seems especially useful. It was therefore necessary in the first stage to identify to which extent the parameters characterizing LPF electroconductivity were capable of adequately reflecting peculiar features of the above processes. To the best of our knowledge based on the analysis of the literature data, no such attempts to study LPF electroconductivity in detail from this standpoint have been made.

The purpose of this work was to establish a relationship of LPF electroconductivity with the processes of its oxygen exchange with the surrounding medium in the course of sintering of this ceramic and its thermal annealing in different media.

EXPERIMENTAL PROCEDURE

The specimens of LPF ceramics were prepared using a standard ceramic-production process [2]. Bismuth teroxide in the amount of 3 wt. % was added to thus synthesized powder. Ferrite workpieces were formed by single-side compaction as pellets measuring 18 cm in diameter and 3mm in thickness, which was followed by their sintering in air at $T = 1373$ K for 4 hours in a furnace with silit heaters. The ceramic material sintered from this furnace mixture exhibited low density ($\rho_p = 4.26$ g/ cm^3). We are going to refer to it as A-type ceramic.

In order to obtain denser specimens, the furnace mixture was subjected to activation by additional processing in an AGO-2 planetary mill for 4 min. The ball-to-hinge mass ratio was 40 and the ball flight acceleration was 20 g. An X-ray
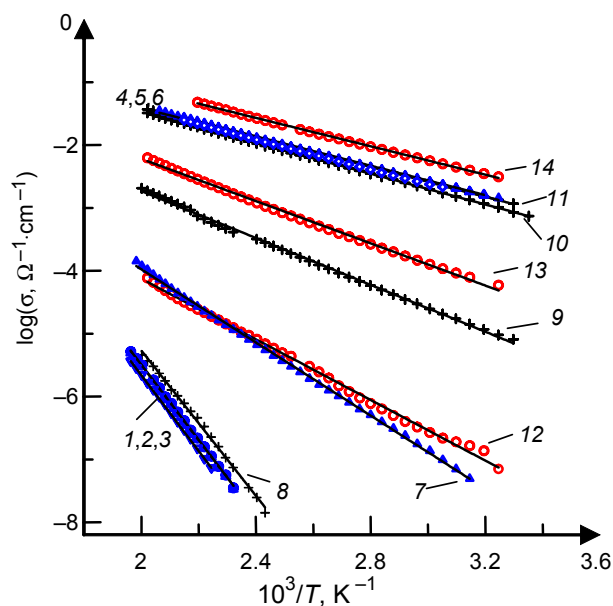
Fig. 1. Temperature dependences of electroconductivity for A-type (curves *1 – 7*) and B-type (curves *8 – 14*) ceramics: after sintering at 0μm (*1*), 170 μm (*2*), and 370 μm (*3*); after annealing at $T = 1023$ K in vacuum at a depth of 0 μm (*4*), 70 μm (*5*), 120 μm (*6*) and subsequent heating in air at $T = 1023$ K for 2h. at 0 μm (*7*); after sintering at 0 μm (*8*), 100 μm (*9*), 300 μm (*10*), 400 μm (*11*); after removing a layer of 400 μm and subsequent annealing in air at $T = 1023$ K for 2h at 0 μm(*12*), 65 μm(*13*) and 185 μm (*14*).

diffraction analysis demonstrated virtually identical diffraction patterns of nonactivated and mechanically activated powders. The mechanical activation of the furnace feed facilitated production of ceramic material of a higher pyctometric density $\rho_p = 4.45$ g/cm^3 (B-type ceramic).

According to the data of X-ray diffraction analysis, the lattice parameter of LPF $a = 8.345$ Å, and its X-ray radiographic density $\rho_x = 4.73$ g/cm^3. The calculated porosities for A- and B-type ceramics of different density were 10.0 and 5.9%, respectively.

Measurements of static electroconductivity were performed in the temperature range $T = 293–523$ K by a spreading resistance technique [3] using a layer-by-layer analysis. This technique allows an analysis of temperature dependences of electroconductivity to be made in thin sub-surface layers at different distance from the specimen surface by successive grinding of these layers. The thickness of the layer under study was about 20–30 μm.

EXPERIMENTAL RESULTS

A-type ceramic

An X-ray diffraction analysis demonstrated that the sintered ceramic was entirely in single-phase state. The diffraction patterns contained superstructure reflections, which is indicative of the presence of a process of 1:3 atomic ordering, as a result of which three ions of Fe^{+3} and one ion of Li are duly located in octahedral positions along the crystallographic directions <110>, and the cationic distribution of Fe^{+3} and Li$^+$ ions between the tetrahedral (A) and octahedral (B) sublattices is the following: Fe^{+3} [Li$_{0,5}$ Fe^{+3} $_{1\cdot5}$] O $_4$ [4].

The temperature dependences of LPF electroconductivity measured after layer–by-layer grinding of the surface layers of the A-type ceramic are given in Fig. 1 (curves *1–3*). It is evident that in the temperature range in question the electroconductivity is exponentially increasing at one value of activation energy E_a. Note that the parameters characterizing

electroconductivity remain the same throughout the entire thickness of the specimen. In the initial state, the sintered specimens were characterized by low electroconductivity but quite high ($E_a = 1.19$ eV) activation energy (Fig. 1).

It is well known [5] that LPF possesses semiconducting properties and is characterized by the *n*-type conduction. The most characteristic property of oxide semiconductors is considerable and quite easily adjustable deviations from stoichiometric compositions of metal and oxygen ions. This gives rise to electrically active centers formed in the crystal lattice of the oxides. On the other hand, a polycrystalline character of the structure of semiconductors results in the formation of potential barriers in the regions of grain boundaries (GB), whose magnitude and properties are largely controlled by different degrees of GB and grain bulk oxidation.

In [6], it was clearly shown by the measurement of static conductivity that the value of E_a in ferrite ceramic was nearly equal to the height of a grain-boundary potential barrier. We, therefore, believe that the value of E_a in polycrystalline LPF obtained from the measurements of static conductivity would also characterize the barrier potential difference. A high value of E_a, and also its nearly uniform distribution with respect to depth, results from effectively running oxidation, giving rise to an increase in the negative charge of the GB interlayer. This is to a great extent favored by insufficient density of the sintered ceramic, as the main channel of oxygen supply is its diffusion along grain- and phase boundaries that are likely to have loose structure in this ceramic.

The dependence of the value of E_a on the oxidized state of the boundary is indirectly supported by the tests on annealing of ceramic specimens in vacuum at $T = 1023$ K for 1 h. The temperature dependences of conductivity of the specimens following this treatment which are given in Fig. 1 (curves *4 – 6*) point to a considerable decrease in electric resistance and value of E_a, with the latter found to be 0.23 eV. Grinding of the surface layers did not give rise to any substantial variations in conductivity. That is to say that reductive vacuum annealing transferred LPF from high-resistance to low-resistance state. A most likely reason for a decrease in E_a is removal of oxygen via the mechanism of GB diffusion into the surrounding medium, which causes a drop in the barrier potential.

Subsequent annealing of the specimens in air at $T = 1023$ K is accompanied by a decrease in conductivity and increase in E_a (Fig.1, curve *7*). It is to be mentioned that vacuum annealing resulted in disappearance of superstructure reflections from the diffraction patterns. Hence it follows that the ordered arrangement of lithium and iron ions in the B-sublattice of LPF had been distorted.

The presence or absence of 1:3 ordering could, in principle, somehow influence the process of electron transfer in LPF. When ordering is distorted, the iron ion population of octahedral positions is higher. One cannot rule out that, given the hopping conduction mechanism, this circumstance could to a certain degree influence the electron transfer in LPF. In what follows we are going to show that order–disorder transitions in the lattice of LPF do not noticeably affect conductivity of ceramic structure.

B-type ceramic

According to the data of X-ray diffraction analysis, mechanical activation of powders did not result in any special features of formation of phase composition of sintered ceramic (B-type ceramic). The crystal lattice of LPF was also characterized by an ordered arrangement of cations in octahedral lattice positions.

In addition to the above findings, while studying conductivity of B-type ceramic we discovered the following peculiarities. Its electrical properties significantly varied over the depth of the pellet specimen (Fig. 1, curves *8–11*). The surface layers exhibited low conductivity and high electron transfer activation energy ($E_a = 1.14$ eV). In a qualitative respect, these parameters were sufficiently close to the values typical of A-type sintered ceramic.

Upon removal of the surface layers by grinding, a natural increase in conductivity and a decrease in the value of E_a (Fig. 1, curves *8–11*) are observed. In the layers in the bulk of the specimen, 400 μm from the surface, $E_a = 0.2$ eV. According to the data of X-ray diffraction analysis, in this case an ordered cationic distribution in the bulk layers of the ceramic is maintained in the lattice. From the data presented in Fig. 1 it is evident that dependences *11* and *14* are quite close to each other. This takes place in spite of the fact that in one case the crystal lattice of LPF was characterized by an ordered cationic distribution (curve *11*), while in the other it was not so (curve *14*). We can therefore make a conclusion that a transition from disordered to ordered spinel is incapable of exerting a significant influence on LPF conductivity.
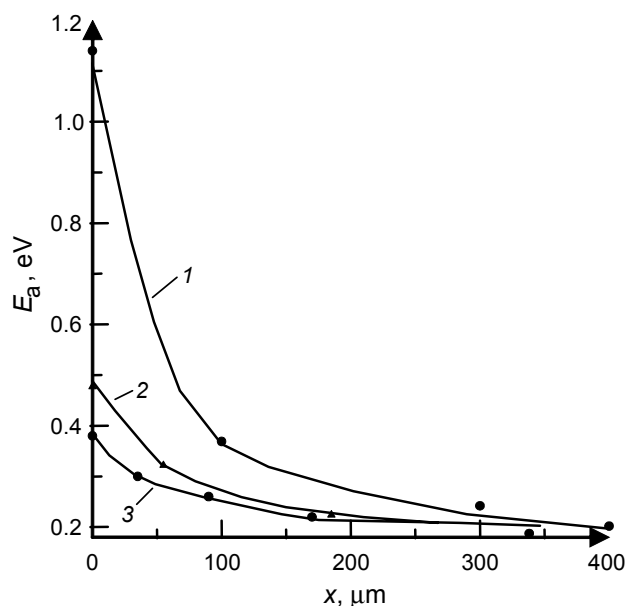
Fig. 2. Distribution of E_a with respect to the depth of a B-type ceramic specimen: after sintering (curve *1*), after removal of a 400 μm-thick layer oxidized in sintering and subsequent annealing runs in air for 2h. at $T = 1023$ and 973 K , respectively (curves *2* and *3*).

A depth-related profile of E_a formed in the course of sintering is shown in Fig. 2 (curve *1*). The nonuniformity of electric properties of B-type ceramic is very likely to be due to nonuniform oxidation of the specimens. This is largely favored by more effective sintering of mechanically activated powders. This produces denser ceramic material and the diffusibility is sharply decreased.

After removal by mechanical grinding of surface layers oxidized in the course of sintering the specimens with uniform distribution of $E_a = 0.2$ eV over the depth were subjected to annealing in air at atmospheric pressure within the temperature range $T = 973–1023$ K for 2 hours. This thermal treatment again resulted in formation of surface layers with nonuniform distribution of properties with respect to depth. The measured depth distribution of $E_a(x)$ after annealing runs is given in Fig. 2. It is evident that with increasing annealing temperature there is both an increase in the surface value of E_a and the length of its depth profile. This is indicative of involvement of diffusion-controlled oxidation processes in the formation of an E_a profile.

According to the concepts developed in this paper, formation of the depth profile of $E_a(x)$ in polycrystalline structures during annealing is related to a change in the value of grain-boundary potential barrier over the specimen depth as a result of diffusion of oxygen from the surrounding medium along grain boundaries and from the latter into the bulk of the gains. Grain-boundary diffusion occurs by a few orders of magnitude faster than that into the bulk. This facilitates accumulation of excessive oxygen at a grain boundary compared to the bulk of the grain. As a result, the potential barrier value increases and the profile of $E_a(x)$ is formed.

To sum up, the following conclusions could be made:

1. The investigations performed testify in favor of the fact that the activation energy of electric conductivity of polycrystalline LPF is a parameter sensitive to its stoichiometry with respect to oxygen.

2. The depth profiles of conductivity activation energy formed in the course of LPF annealing provide evidence to evaluate the efficiency of redox processes and their direction.

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