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The Positive Temperature Coefficient of Resistivity Effect in the Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ Ceramics Admixed with Lithium

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In the paper technological conditions were looked for to obtain the Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ (PFN) ceramics and the PFN ceramics with the lithium admixture with the highest electric conduction and conditions appropriate for the PTC-R effect formation. Measurements of dc electrical resistivity, dielectric permittivity and dielectric loss were made as functions of temperature from room temperature to 190°C, at 1 kHz. The best set of values of dielectric loss and dielectric constant, from the ferroelectricity point of view, were obtained when the precursor with orthorhombic structure was employed. By creating appropriate technological conditions in the PFN ceramics the PTC-R effect can occur above the Curie temperature. Their electric properties are determined by presence of a basic phase of the potential barrier on the grain boundaries.

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1. Introduction

Oxywoctahedral compounds of the perovskite structure and semiconducting properties as far an electric aspect is concerned fall into an intermediate area between typical dielectrics and semiconductors. Thus, they behave as semi-dielectrics or semiconductors with a broad energy gap. A great isomorphism, characteristic for perovskites (easy to deviate from stoichiometry), enables to control physical properties by a selection of technological conditions admixture. The ferroelectric state in the materials of perovskite structure is an effect of a phase transition connected with deformation of regular perovskite cells as a result of cooling of the material to temperatures lower than the Curie temperature.

The PbFe$_{1/2}$Nb$_{1/2}$O$_3$ (PFN) ceramics belongs to a group of the perovskite ferroelectrics with the general A(B′B″)O$_3$ formula, where iron and niobium ions substitute themselves at random into positions B′ and B″, and lead into position A [1, 2].

Posistors is a group of materials having an area of a positive temperature coefficient of resistance α_T, namely materials showing so called the PTC-R effect. A characteristic feature of posistors is a strong increase in their effective resistance from above the T_C Curie temperature. Their electric properties are determined by presence of basic phase potential barriers on the grain boundaries. In the 60-ties of last century, Heywang proposed a description of a PTC-R phenomenon mechanism on a basis of a model of a grain boundary energy structure responsible for a rapid increase in the effective resistance at specific temperatures, on an example of the BaTiO$_3$ ceramics [3].

An objective of this article was to select technological conditions of the PbFe$_{1/2}$Nb$_{1/2}$O$_3$ ceramics admixed with lithium, aiming at decreasing electric conduction and to determine conditions in which the PTC-R effect originates in the lithium admixed PFN ceramics.

2. Experiment

The PFN ceramics obtained by a sintering method from PbO, Fe$_2$O$_3$ and Nb$_2$O$_5$ oxides and specimens containing an admixture of the Li$_2$CO$_3$ lithium carbonate in the amount of 0.5 mol.% (PLiFN1, PLiFN2, PLiFN3) were the test material (Table). Synthesizing of the PFN and PLiFN1 specimens was conducted by a method of powder calcination in the conditions $T_\mathrm{s} = 800$°C for $t_\mathrm{s} = 3$ h, and their compacting as a result of free sintering at the temperature of $T = 1125$°C for 2 h. The remaining two specimens were synthesized as a result of a reaction in the solid phase using a powder mixture compacting method. In this group two specimens were obtained: as a result of a single sintering in the conditions $T_\mathrm{s} = 950$°C/$t_\mathrm{s} = 4$ h (PLiFN2), and as a result of double sintering in the conditions $T_\mathrm{s1} = 950$°C/$t_\mathrm{s} = 4$ h and $T_\mathrm{s2} = 1050$°C/$t_\mathrm{s} = 4$ h (PLiFN3).

Effective resistance tests were conducted in the 20–180°C temperature range by a pico-ammeter (Tesla multimeter BM518), and temperature measurements of dielectric parameters on a capacity bridge of a type QuadTech 1920 Precision LCR Meter.

3. Test results and their discussion

The ρ direct current effective resistance of the non-admixed PFN ceramics at room temperature is $\approx 10^8$ Ω m, and at temperature $T_m = 105$°C $\approx 10^5$ Ω m. Above the T_m phase transition temperature ρ decreases rapidly. While sintering the PFN ceramics with the lithium admixture at low temperature (950°C), there is a decrease in the electric conduction in comparison with

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TABLE
Physical parameters of the lithium non-admixed and admixed PFN ceramics.

| Sign samples	PFN	PLiFN1	PLiFN2	PLiFN3
sintering conditions T_s/t_s	1125°C/2 h		950°C/4 h	950°C/4 h + 1050°C/4 h
ρ_{exp} [g/cm³]	8.08	8.05	8.06	7.26
T_m [°C]	105	98	102	97
ε_r	2860	10060	2760	6450
ε_m	(10480)	(17250)	(8800)	(17910)
$\tan\delta_{Tr}$	0.022	0.335	0.011	0.179
$\tan\delta_{Tm}$	(0.059)	(0.433)	(0.023)	(0.349)
ρ in T_r [Ω m]	1.39×10^8	8.93×10^4	1.61×10^8	2.73×10^5
ρ in T_m [Ω m]	4.21×10^5	3.92×10^3	1.66×10^6	1.28×10^4
E_{Act} in I [eV]	0.402	0.534	0.566	0.456
E_{Act} in II [eV]	0.892		0.669	
E_{Act} in III [eV]	0.926	0.677	0.664	0.506

Fig. 1. Dependences of the direct current effective resistance logarithm on converse of the temperature (a) and temperature (b) for the PFN ceramics admixed with lithium.

the non-admixed PFN ceramics, and their $\rho(T)$ characteristics have a similar course.

The PFN ceramics shows semiconducting properties of n-type connected with deviation from stoichiometry and presence of oxygen vacancies. PFN admixing in the amount of 1.0 at.% Li decreases electron conduction and it changes a character of electrical conduction from n-type to p-type [4].

The Li⁺ lithium cations substituted into the Fe³⁺ iron positions result in forming acceptor centers of which negative electric charges can be compensated by a valence charge in the Pb ion. It is connected with an electric charge jump in the donor band, being the dominant mechanism of conduction in the PFN ceramics admixed with lithium at a low temperature, which is proved by low values of electric conduction [4].

An increase in a temperature of the PLiFN1 and PLiFN3 sintering causes an increase in specimen conduction, and in the area of a phase transition the PTC-R effect occurs, namely an area of a positive temperature resistance coefficient (Fig. 1). According to Heywang's theory, it is connected with presence of a potential barrier on the grain boundaries in the ceramics, forming as a result of compensation of acceptor states on their surface [5]. Effective resistance jump with an increase in temperature in the case of the PLiFN material is not as big as for typical posistors (reaching even to 8 orders).

In the $\rho(T)$ diagram one can be seen that the PTC-R effect for specimens PLiFN1 and PLiFN3 admixed with lithium is observed only above the phase transition temperature. According to Jonker's model it is connected with the complete compensation of the surface states by the (P_S) spontaneous polarization formed in each semiconductor grain at T_C and it is connected with a phase transition from the paraelectric phase to a ferroelectric phase, in which the Schottky barrier is damped by spontaneous polarization of domains adjacent to the grain boundary [6]. A negative charge compensating ionized donor levels is formed on the grain boundary surface,
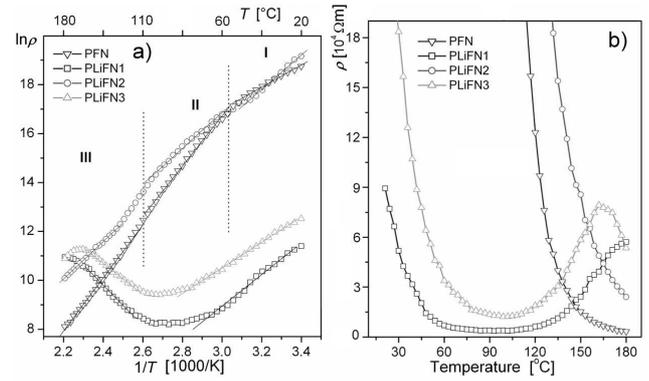
and lack of potential barriers on those boundaries facilitates formation of paths conducting through the ceramics which causes its low effective resistance at room temperature [6].

Activation energy for the specimens in question (Table) was calculated according to Arrhenius' law

$$\rho = \rho_0 \exp\left(\frac{E_{Act}}{k_B T}\right), \qquad (1)$$

where ρ_0 — pre-exponential factor, k_B — Boltzmann's constant, T — absolute temperature, E_{Act} — the activation energy appointed from the slope of $\ln\rho_{DC}$ vs. $1/T$ plot.

The permittivity $\varepsilon(T)$ (a) and a tangent of the dielectric loss $\tan\delta(T)$ (b) temperature dependences (at $\nu = 1$ kHz) for the PFN ceramics specimens in question are presented in Fig. 2. Lithium added to the base composition of the $Pb(Fe_{1/2}Nb_{1/2})O_3$ causes a slight displacement of the phase transition toward lower temperatures. High sintering temperatures of the admixed specimens increase values of the ε_m maximum permittivity and a character of a course of dielectric losses.
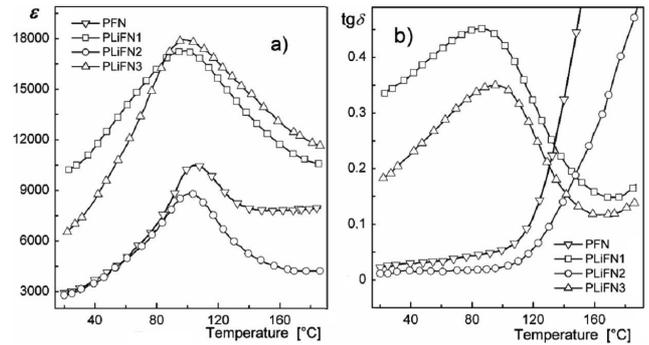

Fig. 2. Dependences of ε permittivity (a) and a tangent of the dielectric loss angle (b) in the temperature function for the admixed PFN ceramics with the lithium admixture ($\nu = 1$ kHz).

For the non-admixed PFN ceramics and for composition PLiFN2 above temperature T_m, there is a rapid increase of dielectric losses which can be connected with a partial reduction of the $Fe^{3+} \leftrightarrow Fe^{2+}$ ions in the octahedral positions and formation of oxygen vacancies during the sintering process [7, 8]. In case of specimens sintered at higher temperatures (PLiFN1, PLiFN3) losses are higher and they increase quickly from the room temperature. While approaching a phase transition dielectric losses begin to decrease until the temperature of about 160°C, and above it they increase again, but not as rapidly as in the case of specimens without the PTC-R effect.

4. Summing up

In the $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics the Fe iron ion in the valence state is sensitive to sintering conditions and it plays an important role in causing anomalous behaviour of effective resistance [5, 9, 6]. The non-admixed PFN ceramics shows electron conduction of n-type (with dominance of anion vacancies) [10, 11]. Addition of small amounts of lithium into PFN (1.0 at.%) and use of low temperatures of sintering compensate partially conduction of the n-type and change a character of the conduction into p-type [4].

An increase in the temperature of PLiFN sintering results in occurrence of the PTC-R effect in the areas of the phase transition. The higher sintering temperature the more distinctive PTC-R effect is. The specimens showing the PTC-R effect have higher values of the maximum permittivity.

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