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Applications of iron (III) nitrate to obtain the multiferroic $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics by the sol–gel method

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ABSTRACT

In the present work the results of preparation of the multiferroic $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics were presented. A synthesis of the PFN ceramics powders was carried out via a wet chemical route, by the sol–gel method. The densification process of ceramic powders was made by using the free sintering method (a conventional sintering) or by the hot uniaxial pressing method.

Measurements of the SEM micrographs of fracture surfaces, dielectric and electric conductivity properties were performed. The investigations have shown the influence of densification process on the microstructure and physical properties of ceramics obtained in such a way, as well as usable parameters and a character of electric conductivity on which PFN is dependent.

1. Introduction

Multiferroics are materials of ferroic properties, which show simultaneously at least two types of physical states. For example: a ferromagnetic state (antiferromagnetic, ferrimagnetic) a ferroelectric state (antiferroelectric, ferrielectric), or a ferroelastic state (ferromagneticelastic, ferroelastoelectric). The multiferroics are characterized by higher intelligence, which is manifested by the fact that they react to external factors, such as the magnetic, electric, elastic or thermal influence [1]. In those types of materials the spontaneous magnetization M_s, the spontaneous polarization p_s or the spontaneous deformation η_s can be changed both by the magnetic field H and the electric field E or the stress σ [2]. The ferroelectromagnetic $PbFe_{1-x}Nb_xO_3$ ceramics, shortly called PFN, is a material which belongs to a group of multiferroics [1,3–7]. It has a structure of the perovskite type with the general formula ABO_3 where in the elementary cell positions A are occupied by a big lead ion Pb, whereas positions B are occupied by iron ions Fe and niobium Nb alternatively [8–10].

On the basis of ferroelectromagnetics, used in highly advanced electrotechnology, it is possible to build elements of both ferromagnetic and ferroelectric memories, simultaneously electrically controlled ferromagnetic resonance systems and transducers with magnetic modulated piezoelectricity. Those materials are also used to build adjustable transducer, electrostriction servo motors and micro-regulators, sensors, detectors, etc. [11–13]. Ferroelectromagnetics in such equipment are used mainly in a form of volumetric or thin layer ceramic elements.

The ceramics properties depend significantly on a way of its manufacturing beginning with a synthesis of component powders (selecting an appropriate way of synthesizing) through their mixing, refining, compacting or final sintering. Convenient and effective conditions of the ceramic powder synthesis are provided by the sol–gel method [11,14]. It is based on reactions in solutions of precursors—organic or inorganic metal salts of high purity. Organic metal salts (acetates, alcoholates) or inorganic compounds (e.g. nitrates, metal hydroxides) can be initial materials to prepare a chemical solution. The reaction products of the initial components are besides, e.g. complexes of alcoholates also esters removed from the medium by a simple distillation, as by-products. In the sol–gel technology an appropriate solvent is added into the solution and external ligands (stabilizers) in order to increase stability of alcoholic solutions. Hydrolysis is a next stage of the sol–gel method. As a result of hydrolysis reactions, sol (colloidal solution with a liquid dispersion medium) is formed. If an organic liquid is a dispersion medium, organosols will be formed, if it is water, hydrosols will be formed. As a result of the mutual interaction between sol particles, the colloidal system losses its fluidity it gelatinizes. Gels containing a liquid dispersion medium, namely lysogels (hydrogels, organogels) are subjected to a drying process and change into xerogels, being a synthesised powder material of the given material.

The sol–gel technology has a lot of advantages, among others, it provides perfect homogeneity of the component powders, it lowers

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a temperature of component synthesizing, and it does not require use of expensive and complicated equipment. Powders for the PFN ceramics production were obtained by the sol–gel method in this work and an influence of a densification method on the basic properties of the PFN ceramics was examined.

2. Experimental

The $PbFe_{1-x}Nb_xO_3$ (PFN) ceramics was obtained as a result of a powder synthesis by sol–gel method using as precursors lead (II) acetate trihydrate pure p.o. $Pb(CH_3COO)_2·3H_2O$ (POCh), iron (III) nitrate nonahydrate pure p.o. $Fe(NO_3)_3·3H_2O$ (POCh), nobium ethylate-niobium (V) ethoxide $Nb(OC_2H_5)_5$ 99.95% (Aldrich). Since to the reaction medium lead is supplied in a form of the ($Pb(COOR)_2$) carboxylic acid salt, it was added in excess because of its low evaporation temperature. In the sol–gel process 2-metoxyethylate was a solvent, and acethyloaten was a stabilizer, which was used both to control a hydrolysis of alcoholates and to protect against too quick gelation of the solution. Distilled water was used for the hydrolysis reaction (a specific case of the solvolysis).

2.1. A course of the PFN ceramics technological process

The lead acetate weighed in a stoichiometric way was solubilized in the 2-methoxyethylate by mixing and heating the solution in the heating jacket. The clear and colourless solution was obtained. The iron nitride and the niobium ethylate were weighed in a similar stoichiometric way and were solubilized in 2-methoxyethylate; a solution of brown colour was obtained in the first case and a bright yellow solution in the other.

The next stage of the technology was to mix three solutions obtained. That process was conducted by mixing the components, with their simultaneous heating in the heating jacket. It resulted in obtaining a brown solution to which the acetylacetone was added as a stabiliser. The solution became brown. Then, distilled water was added to start a hydrolysis process. It begins a sol formation process. The sol formed underwent gelation quickly (gel precipitated in a form of longitudinal needles on the surface). In order to accelerate gelation and to change the gel into a powder the solution was annealed under the IR lamp. The PFN powder obtained after drying was mixed and baked in a furnace at temperature $T_w = 600\,^{\circ}C$ for $t_w = 2$ h to remove organic parts.

After baking organic parts the powder was mixed and pressed into compacts. Densification was made by two methods: free sintering in the conditions: $T_s = 1050\,^{\circ}C/t_s = 2$ h (FS1) and $T_s = 1100\,^{\circ}C/t_s = 2$ h (FS2) or a hot uniaxial pressing method (HUP) in the conditions: $T_s = 1050\,^{\circ}C/t_s = 1$ h$/p_s = 20$ MPa (HUP1) and $T_s = 1100\,^{\circ}C/t_s = 1$ h$/p_s = 20$ MPa (HUP2). The course of the PFN gelation is presented in Fig. 1.

The ceramic microstructure examinations were made by a HITACHI S-4700 scanning microscope (SEM) and the EDS Noran Vantage system. For electric measurements electrodes were put on the specimen surface by the silver paste baking method. The temperature measurements of dielectric properties were made on a capacity bridge of a QuadTech 1920 Precision LCR Meter type, and a pA meter (Tesla multimeter BM518) was used for direct current resistance. The PFN physical parameters with specimen markings and baking conditions are presented in Table 1.

3. Results and discussion

The microstructure and crystalline structure of the ceramics depend on a lot of factors, among others, a technological process, types of basic materials, the phase transition kinetics, grain growth conditions, a method of the ceramic powder synthesizing, time and a way of their compacting, etc. A technology of ceramic production has a direct influence on density, a crystalline structure and a microstructure of the ceramics, which decide about later properties and applied parameters.

Microstructure images of the PFN ceramics specimen fractures are presented in Fig. 2. Analyzing the obtained SEM images it can be found that the PFN ceramics obtained from the powder synthesized by the sol–gel method is characterized by a dense structure with a small grain. The PFN ceramics free sintered at low temperature (FS1) show the lowest grain homogeneity, with high porosity what results in a decrease of the specimen density. An increase in the sintering temperature (FS2) favours the good grain growth, allowing correct homogenization of the microstructure and their good formation, and a short sintering time hinders the excessive grain growth. Those conditions favour a decrease in porosity improving the ceramic density.

Characteristics of the direct current conductivity in a form of $\ln\rho(1/T)$ (a) and $\rho(T)$ (b) diagrams are presented in Fig. 3. It can be observed that a method of powder compacting has an influence on a character of the electric conduction of the PFN ceramics.

In a case of free sintered specimens with the increase of temperature the direct current specific resistance decreases until the phase transition temperature. Such characteristic behaviour is typical for

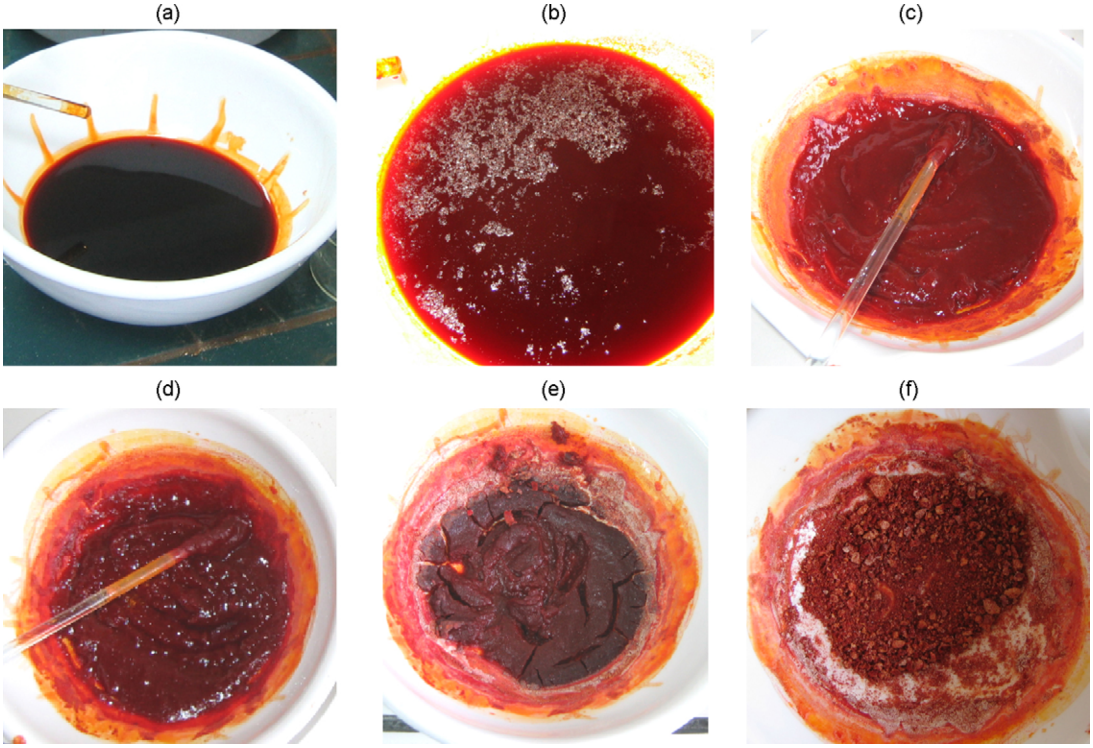

Fig. 1. The PFN gelation: (a) sol, (b) gelation beginning, (c and d) the gelation process after 1 day, (e) the hydrogel after 2 days, and (f) the xerogel form—the dry PFN powder.

Table 1
Parameters of the PFN ceramics obtained by the sol–gel technology (a cooling cycle).

Sintering conditions	FS1 $T_s = 1050\,^\circ\mathrm{C}/t_s = 2\,\mathrm{h}$	FS2 $T_s = 1100\,^\circ\mathrm{C}/t_s = 2\,\mathrm{h}$	HUP1 $T_s = 1050\,^\circ\mathrm{C}/t_s = 1\,\mathrm{h}/p_s = 20\,\mathrm{MPa}$	HUP2 $T_s = 1100\,^\circ\mathrm{C}/t_s = 1\,\mathrm{h}/p_s = 20\,\mathrm{MPa}$
ρ_{exp} [g/cm^3]	6.90	7.88	7.43	7.26
T_m [°C]	105	99	99	98
ε_r	2,860	33,800	8,000	5,900
$(\mathrm{tg}\delta)_{T_r}$	0.22	0.65	0.80	0.22
ε_m	7,070	40,500	19,960	11,840
$(\mathrm{tg}\delta)_{T_m}$	0.47	1.14	1.31	0.39
$\varepsilon_\mathrm{m}/\varepsilon_r$	2.47	1.66	2.49	2.00
E_{Act} in I [eV]	0.334	0.227	0.129	0.192
E_{Act} in II [eV]	0.673	0.656	1.304	0.979
ρ_{DC} in $T_r \times 10^5$ [Ω/m]	1.48	0.073	0.16	3.62
ρ_{DC} in $T_m \times 10^4$ [Ω/m]	1.61	0.18	0.59	9.92
α	1.76	1.77	1.70	1.84
C	0.85	10.90	3.04	4.05

materials with a negative temperature coefficient of resistance (the NTC-R effect). Further increase in temperature causes the presence of anomalies in a form of a slight increase in the specific resistance, and then it decreases further. In a case of the specimens densification by the hot uniaxial pressing method from the room temperature to the phase transition temperature, there is a decrease in the specific resistance as in the previous case. At further temperature increase above the phase transition an increase in the specific resistance is visible until the temperature of about 175 °C (FS1) and about 200 °C (FS2), what is characteristic for materials having a positive temperature coefficient of specific resistance (the PTC-R effect). Further increase in temperature causes that the specific resistance decreases again.

The temperature relationships of electric permittivity for the PFN ceramics compacted by FS and HUP methods are presented in Fig. 4. The PFN ceramics obtained by the sol–gel method have high values of the maximum electric permittivity, and the phase transition from the ferroelectric to paraelectric phase has a diffuse character. This wide temperature range of the phase transition is connected with the structure ordering (with the non-uniform distribution of Fe and Nb ions in the unit cell). This non-uniform distribution of iron and niobium in positions B of the compound leads to forming of microscopic areas with different Curie temperatures. The lower degree of ordering is, the phase transition from the ferroelectric into paraelectric phase takes place in a wider temperature range.

The character and degree of the phase transition diffusion can be determined by a lot of ways. For example, as a ratio of the maximum electric permittivity to the electric permittivity at room temperature ($\varepsilon_m/\varepsilon_r$) or on basis of the relationship (1):

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = C(T - T_m)^\alpha, \tag{1}$$

where ε_m, electric permittivity at temperature T_m; C, constant, α, exponent showing a degree of the diffusion of the change from the ferroelectric to paraelectric phase; T_m, a temperature at which

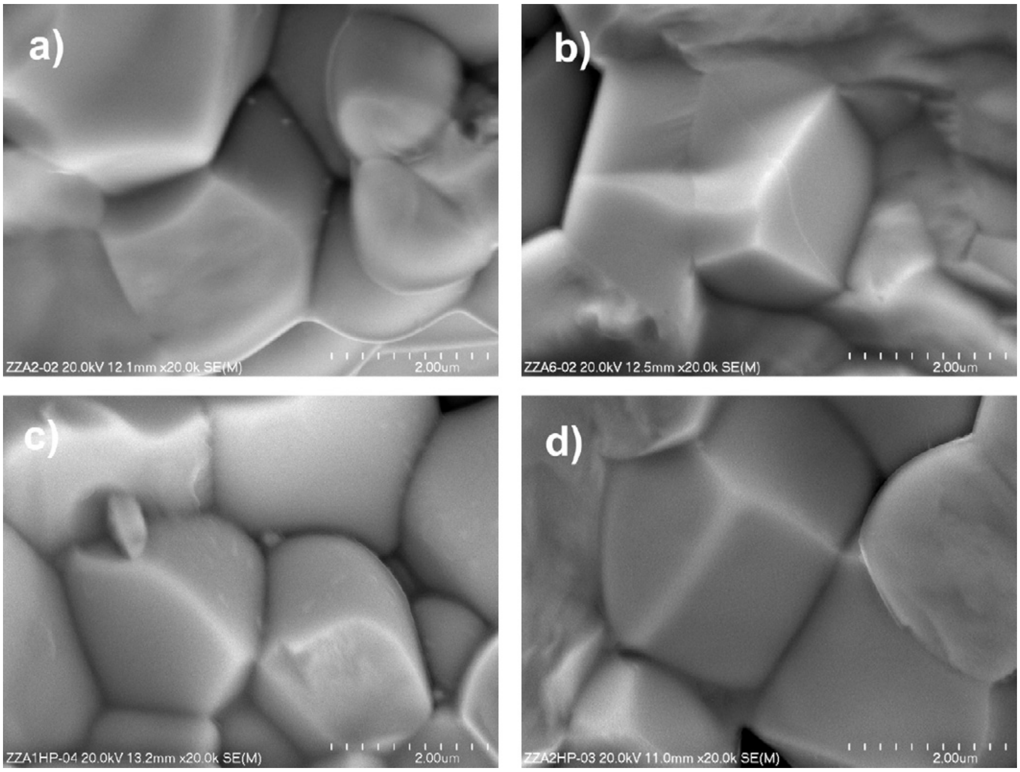

Fig. 2. The SEM photographs of the fracture microstructure of the PFN ceramics obtained by the sol–gel method: (a) FS1, (b) FS2, (c) HUP1, and (d) HUP2 (magnification 20,000×).

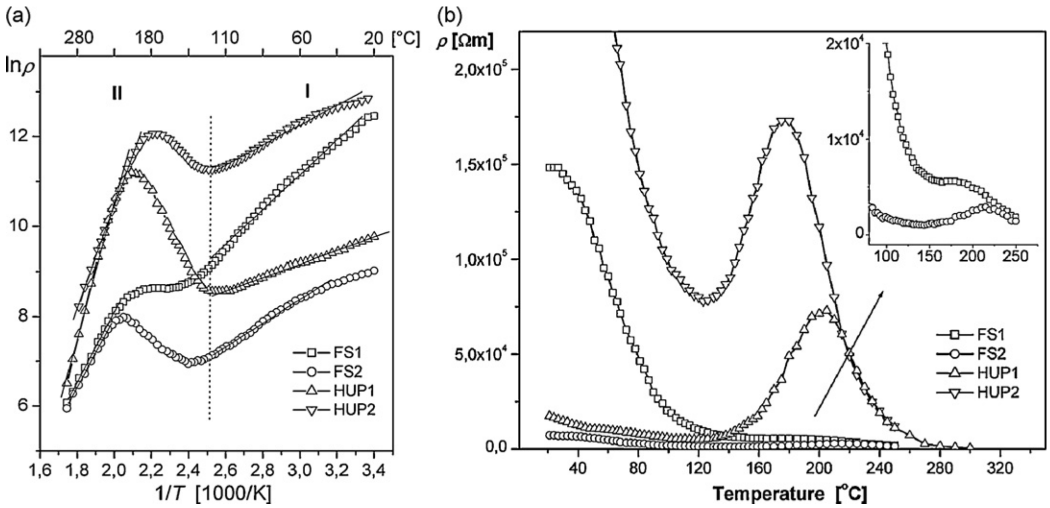

Fig. 3. Logarithmic dependences of the direct current specific resistance on the temperature inverse ($1/T$) (a) and ρ on a temperature (b) for the ceramics PFN.

the electric permittivity reaches maximum (ε_m). When a value of the exponent is $\alpha = 1$, it shows behaviour in accordance with the Curie–Weiss law, when $1 < \alpha \leq 2$ the phase transition has a diffuse character [12]. The calculated values of the diffusion exponent α and constant C are presented in Table 1.

Comparing the PFN ceramics specimens obtained in different technological conditions it can be stated that the specimen compacted by the free sintering at the lowest temperature (FS1) has the highest degree of the diffusion phase transition.

A cumulative diagram of the dielectric loss tangent in the temperature function for the examined PFN ceramics specimens is presented in Fig. 5. Like for the direct current conduction courses, similar regularities in the character of the dielectric loss changes can be observed. To the phase transition temperature an increase in the dielectric losses is observed, then their decrease, and next once again an increase occurs but it is a rapid one this time. In the PFN ceramics to the phase transition temperature (in the ferroelectric phase) there are losses for re-polarization, whereas above it (in the paraelectric phase) for the electric conduction.

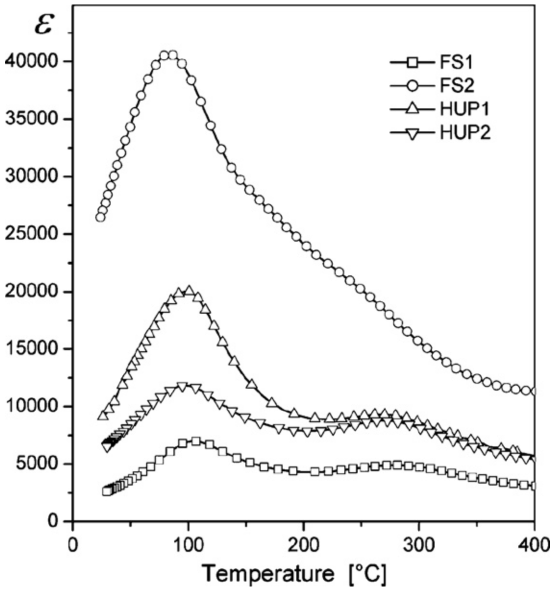

Fig. 4. The ε electric permittivity relationships in the T temperature function for the PFN ceramics obtained by the sol–gel technology ($\nu = 1$ kHz).

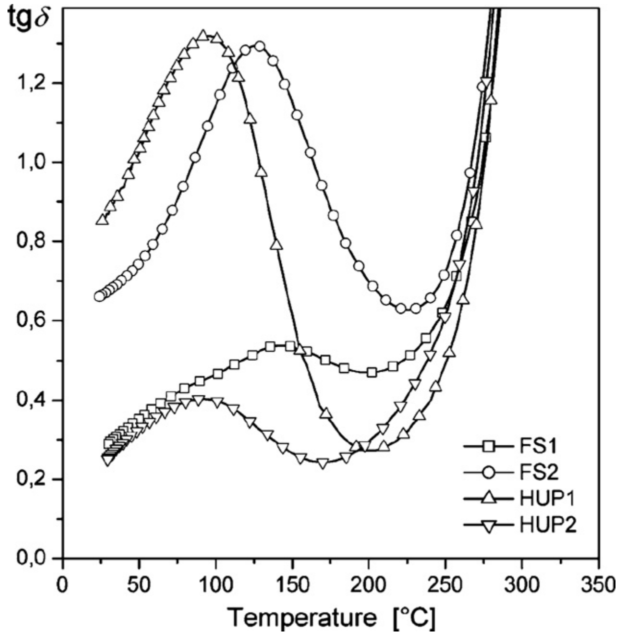

Fig. 5. Relationships of the tgδ–tangent of the dielectric loss angle in the T temperature function for the PFN ceramics obtained by the sol–gel technology.

4. Conclusion

A synthesis method of powders, their structure and properties, a degree of refinement, and also a way of compacting have a significant influence on an appropriate course and a final result of the sintering process in the PFN ceramics technology.

The sol–gel technological process to obtain the $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) ceramics has been presented in the work. The examinations showed that the PFN ceramics, in spite of presence of low amount of the pyrochlore phase, had a densely packed and fine-grained microstructure, and showed high values of electric permittivity. Tests of the direct current specific resistance in the obtained specimens revealed presence of the PTC-R effect in the areas of the phase transition, namely an area with a positive temperature coefficient of resistance. The specimen densification by the hot uniaxial pressing method shows the highest resistance jump.

The examination results presented prove that an appropriate selection of technological conditions at free sintering of the PFN ceramics enables to obtain a product with good dielectric properties.

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