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Electrical Physical Properties of Nanostructured Ferroelectrics in Pulsed Power Electric Fields

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Experimental studies of the electrical physical properties of nanostructured ferroelectrics based on barium-strontium titanate in pulsed power electric fields are described. A setup for carrying out such studies, providing application of voltage impulses with sub-microsecond front durations and amplitudes up to 20 kV to samples of ferroelectric ceramics has been elaborated. This setup enables maintenance of the assigned temperature of samples in the range from room temperature to 70 °C. It follows from carried investigations that nanostructured samples made by sintering of fine-grained barium -strontium titanates doped with zirconium powders having grain sizes order of tens of nanometers show bigger values of dielectric permittivity nonlinearity degree at impulse polarization than those made of powders with most of particle sizes greater than microns.

Keywords: Nano-sized powders, Ferroelectric ceramics, Dielectric permittivity, Nonlinear parameters.

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1. INTRODUCTION

Ferroelectrics are characterized by high dielectric permittivity and presence of a dielectric hysteresis. This stimulates their widespread usage in many areas of technology: radio engineering, electro-acoustics, quantum electronics and measurement technology [1]. Usage of nano-structured powders as feed-stock improves significantly the dielectric parameters of these materials [1].

The electromagnetic wave profile is distorted at its propagation in a medium with nonlinear permittivity. In this case, if discontinuities of the solutions of equations describing electromagnetic waves propagation occur, formation of shock electromagnetic waves (SEMW) may appear [2]. Carried experimental studies [3] have shown the advantages of shock electromagnetic waves usage to obtain steep differences in waves fronts and short current impulses. When ferrites were used as a working medium of forming lines (FLs), wave fronts of the order of 1-5 ns were achieved with voltage amplitude up to 30 kV [3]. Levels of containing ferromagnetic media FLs impulse currents amplitudes are limited because of their rather big inductance and therefore wave resistance. To get bigger current levels it is necessary to increase voltage levels in a line up to the FL insulation electrical strength. The advantage of ferroelectric usage as in comparison with ferromagnetic is a possibility of TLs creation with a much lower wave resistance. As a consequence, it becomes possible to obtain larger currents in a load at applying lower levels of voltage impulses amplitudes.

To generate shock waves in a FL with ferroelectric working media it should have a sufficiently strong nonlinear dependence of permittivity on the applied voltage level, low dielectric losses and a short relaxation time. In addition, the material should have high electrical strength. Therefore, to obtain ferroelectric materials with assigned electrical physical properties, when working out a technology of their synthesis, it is necessary to use a method for studying their properties at different values of the applied voltage over a wide range of frequencies. As the electrical physical characteristics of non-linear working media, as a rule, have strong temperature dependence, the experimental techniques for testing these characteristics should provide an accurate temperature measurement and reproduction of the assigned temperature conditions.

Investigation of the ferroelectrics electrical physical properties in strong electric fields (EFs) causes technical difficulties. Thus, such materials have dielectric losses, causing their non-uniform heating, as well as a strong dependence of the permittivity on temperature. Experimental studies of the nonlinear dielectrics parameters is complicated also because the permittivity nonlinearity is most pronounced in many cases only in electric fields close to the zone of statistical dispersion of the dielectrics electrical strength.

So, to apply such materials in FLs, in most cases it is proper to use them at temperatures slightly higher than the phase transition temperature (above the Curie point) [4]. At such a condition, a rather strong nonlinear dependence of the permittivity on the applied voltage still remains, but the material domain structure is close to destruction, which leads to a sharp decrease of the dielectric losses.

The resonance methods of the nonlinear dielectrics characteristics investigation are widely used [5]. They are suited well for determining of the complex dielectric permittivity, however, they are practically not suitable for investigation of the dynamic dielectric permittivity over a wide frequency range. In this case, application of the Sawyer-Tower scheme in the traditional form [6] is also impossible, because large dielectric losses in ferroelectrics in the ferroelectric phase cause significant heating of a sample, which in turn leads to changing of dielectric permittivity level or even a phase transition in the solid structure. Besides, because of the large dielectric permittivity typical for ferroelectrics, the samples capacity is about units of nanofarad (for smaller capacity values, the required degree of EF homogeneity in a sample cannot be achieved). In the radiofrequency range, such a capacitance is a significant reactive load for AC voltage source used in the Sawyer-Tower scheme.

It is known that usage of ferroelectric ceramics, got by sintering from a coarse grinding raw material does not ensure their nonlinear characteristics at fast growing pulsed EFs application [1]. A possibility of usage for such applications of nanostructured ferroelectric ceramics, obtained from raw materials with submicron granules sizes and at short sintering times, requires additional studies. It is also necessary to determine whether such materials have sufficient electrical strength to withstand high-voltage pulsed influences without breakdown.

The aim of the work is investigation the nanostructured ferroelectrics electrical physical properties in the pulsed mode operation with the help of the developed experimental setup.

2. EXPERIMENTAL SETUP FOR INVESTIGATION OF THE ELECTRICAL PHYSICAL PROPERTIES OF NANOSTRUCTURED FERROELECTRICS AT APPLICATION OF PULSED ELECTRIC FIELDS

The SEMW forming process is non-stationary, and information on the properties the ferroelectric media at time moments, corresponding to the transition polarization curve is required for its description. This necessitates experimental investigations of the ferroelectrics pulsed polarization in strong EFs. For this purpose, experimental studies of the ferroelectric ceramics pulsed polarization at different rates of monotonic increase of the electric field strength in samples were carried out.

Investigation of the dependence of the electric displacement (D) on the electric field strength (E) in the submicrosecond range of the applied EF strength impulse front durations was carried out using Sawyer-Tower scheme [6], which was modernized to apply in the impulse mode operation (see Fig. 1).

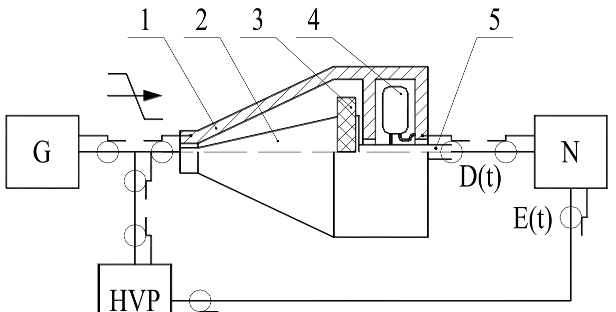

Fig. 1 – Setup for synchronous oscilloscoping of electric field strength and electric displacement in ferroelectric ceramics samples at pulsed polarization. G is pulsed generator of monotonically increasing voltage; HVP is high voltage probe; N is two-channel oscilloscope; 1 is casing; 2 is high-voltage electrode; 3 is ferroelectric ceramics sample; 4 are measuring capacitors; 5 is intermediate electrode, output of $D(t)$ channel

In accordance with Sawyer-Tower method, an investigated sample and a measuring capacitor were connected in series. High voltage of negative polarity was applied to sample of investigated nonlinear dielectric 3. This voltage, monotonously increasing on the impulse front, propagates along the conical line, formed by the inner surface of casing 1 and high-voltage electrode 2. Samples of ferroelectric ceramics $Ba_{1-x}Sr_xTi_{1-y}Zr_yO_3$ in electric field E = 1-5 MV/m were investigated. Samples of the ferroceramic had cylindrical shape. Copper electrodes were deposited on the flat surfaces of the samples by the method of magnetron sputtering. The ratio of the cylinder height to its diameter did not exceed 0.1, which enables obtaining close to the homogeneous EF strength distribution in the samples. The electric field strength magnitude in a sample was determined as the ratio of the voltage on the sample to its height, and the voltage was measured with a capacitive-ohmic high voltage probe (HVP) connected in parallel with the Sawyer Tower circuit. Linear measuring capacitors 4 in Sawyer Tower scheme are arranged in a circle coaxially with connected to them intermediate electrode 5, contacting with the sample low-voltage electrode and with the channel $D(t)$ output. Eight connected in parallel capacitors with insulation from a synthetic film with a low inductive connection of their plates to the terminals were used.

To study the ferroelectrics dielectric permittivity dependence versus temperature, Sawyer-Tower scheme and a sample installed in it, was placed in a thermostatic chamber. The temperature in the chamber was set in the range from 20 °C to 70 °C. Control and measurement of the specified sample temperature levels were carried out with the help of the UDS 12.R DS thermostat with digital temperature sensor DS18B20 TUBE (DALLAS Semiconductor). From the point of view of research aimed at new nonlinear wave systems creating, study of the dielectrics properties in the temperature range from several degrees below to several degrees higher than the phase transition temperature corresponding to a solid state structure transformation from ferroelectric phase is of primary interest. In this range, a strong nonlinearity of dielectric permittivity is observed, and dielectric polarization losses are comparatively low.

The measuring unit of the setup (see Fig. 1) is completely shielded by metal casing 1 and is a sealed coaxial system. Such a design permits reducing of the electromagnetic disturbances influence occurring when pulse generator G is triggered and lessening the parasitic inductances of Sawyer-Tower circuit elements. The setup measuring unit is equipped with coaxial high-frequency terminals for measured parameters $E(t)$ and $D(t)$ oscilloscopic recording. Synchronous recording of voltages proportional to E and D was carried out by a two-channel oscilloscope Tektronix TDS 1012B. As a result of numerical processing of signals recorded by a digital oscilloscope, the dependences of electric displacement, as well as relative and differential permittivity are obtained for the studying samples, depending on the level of the applied electric field strength.

To form a monotonically increasing voltage on the samples of the studied nonlinear dielectrics, an artificial double-forming Blumlein line was used [7]. The Blumlein scheme is very effective for an increasing voltage generation on samples of ferroelectrics at their pulsed polarization studying as it permits generation of power electric field pulses with a smooth front. A Blumlein scheme switch is located on the opposite to a load end of one of the artificial FLs, rather than in a close proximity to it (which differ to a single-forming line switch). Therefore, an impulse noise that occurs when the switch is triggered, outruns the front of the initial impulse on the delay time t_d:

$$t_d \approx N\sqrt{L_l C_l}\ ,$$

where N is number of the line elements; L_l, C_l are inductance and capacitance of each line element correspondingly.

Such a setup design enables investigation of the pulsed ferroelectric ceramics samples polarization in the range of durations of electric field strength growth $\tau_f = 10^{-6}$-10^{-8} s.

To ensure the coaxial measuring unit elements electrical strength, sufficient for carrying out experimental studies at levels of the applied to samples voltages up to 10 kV, a sample of the investigated dielectric was placed in a dry condenser oil. To avoid occurrence of electrical discharges in the pores of ceramic and electrical breakdown along its surface, samples were subjected to vacuum impregnation in transformer oil at 42 °C.

3. ELECTRICAL PHYSICAL PROPERTIES OF NANOSTRUCTURED FERROELECTRICS

At the experiments, negative voltage impulses were applied to investigated samples, as it is easier to provide necessary insulation strength of the high-voltage setup elements for this polarity. Besides, it enables increasing the electrodes area due to reducing samples edges and enhance due to this the degree of EF uniformity in the investigated dielectric working area.

Typical oscillograms of the signals proportional to the electric field strength $E(t)$ and electric displacement $D(t)$ in the nanostructured ferroelectric ceramics samples obtained at different temperature values and assigned shape of impulses of the applied voltage are shown in Fig. 2.

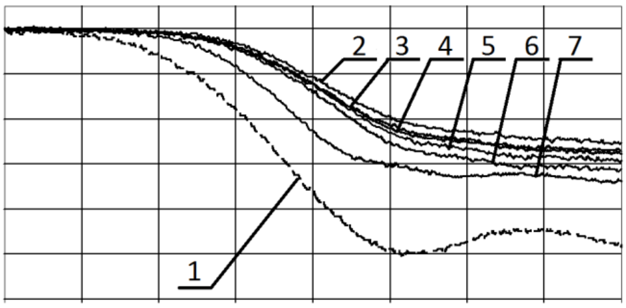

Fig. 2 – Typical oscillograms ($5 \cdot 10^{-8}$ s/div) of the EF strength and electric displacement in $Ba_{0,75}Sr_{0,25}Ti_{0,95}Zr_{0,05}O_3$ ceramic samples. Curve 1 corresponds to EF strength ($3.2 \cdot 10^5$ (V/m)/div); curves 2-7 correspond to electric displacement ($4.29 \cdot 10^{-1}$(C/m^2)/div) in a sample at temperatures 25.8 °C, 30 °C, 35 °C, 40 °C, 45 °C, 55 °C correspondingly

At an impulse front duration of 100 ns for the samples made of $Ba_{0.8}Sr_{0.2}TiO_3$ nanostructured ceramics, the maximum nonlinearity coefficient of the differential dielectric permittivity was observed at 45 °C and maximum electric field strength of 2 MV/m (5 kV on a sample). The nonlinearity coefficient at the same temperature is maximal at 1.2 MV/m electric field strength (3 kV on a sample) for $Ba_{0,75}Sr_{0,25}Ti_{0,95}Zr_{0,05}O_3$ ceramic samples.

The results of measurements using a digital oscilloscope were recorded. A software for primary experimental data processing and getting the dependences of differential dielectric permittivity and electric displacement of the investigated ferroelectric ceramics samples on the strength of the applied to them electric field was elaborated.

Calculation of the electric field strength $E(t)$ and electric displacement $D(t)$ was carried out as follows:

$$E(t) = \frac{U_{Cx}(t)}{d}\ ;$$

$$D(t) = \frac{C_m \times U_{Cm}(t)}{S}\ ,$$

where $U_{Cx}(t)$, $U_{Cm}(t)$ are the results of oscillography of voltages on the capacitances C_x and C_m at the corresponding time moments; C_x and C_m are capacitances of a sample and measuring capacitors; d is an investigated ferroelectric ceramics sample thickness; S is an area of the sample's electrodes.

The obtained experimental oscillograms are not smooth enough for direct numerical derivation because of influence of the interferences, induced in the measuring path. This interferences influence is especially pronounced at calculating of a sample's differential permittivity, as increase of $U_{Cx}(t)$ and $U_{Cm}(t)$ values at one step of the oscilloscope digitization in time domain is comparable with the interference voltages. It is not possible to perform calculations directly by these values, as even small fluctuations in the experimental curves lead to significant errors in their numerical differentiation. So for the carried calculations, the primary experimental data were smoothed out by polynomials of the 15-th degree. Dependences of the differential dielectric permittivity on the applied electric field strength were got by analytical differentiating of the obtained polynomial.

As a result of the voltage signals from $D(t)$ channel numerical processing, the dependences of the relative dielectric permittivity

$$\varepsilon(E) = (1/\varepsilon_0)\cdot(D/E)$$

and differential dielectric permittivity

$$\varepsilon_d(E) = (1/\varepsilon_0)\cdot(\partial D/\partial E)$$

on the electric field strengths were got for the investigated nonlinear dielectrics.

To simulate the process of SEMW formation, the values of digital oscillograms were used, which corresponded to an impulse front taken at a level of 0.1-0.9 from its amplitude value. Typical experimentally obtained dependences of electric displacement and permittivity on the strength of the applied electric field for samples of nanostructured ferroelectric ceramics $Ba_{0,75}Sr_{0,25}Ti_{0,95}Zr_{0,05}O_3$, obtained at different temperatures, are shown in Fig. 3, 4.

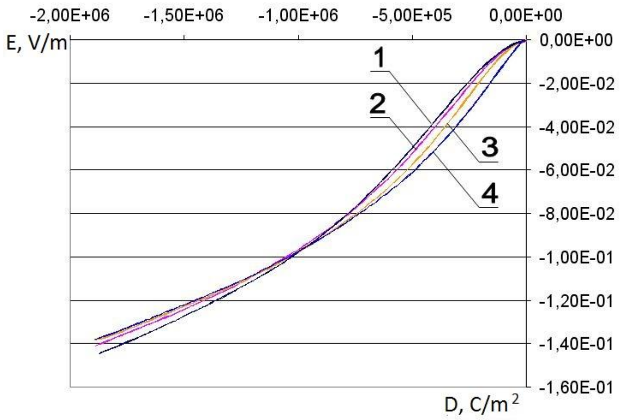

Fig. 3 – Dependence of the electric displacement on the strength of the applied electric field (sample $Ba_{0,75}Sr_{0,25}Ti_{0,95}Zr_{0,05}O_3$). 1 – 24 °C; 2 – 35 °C; 3 – 55 °C; 4 – 45 °C

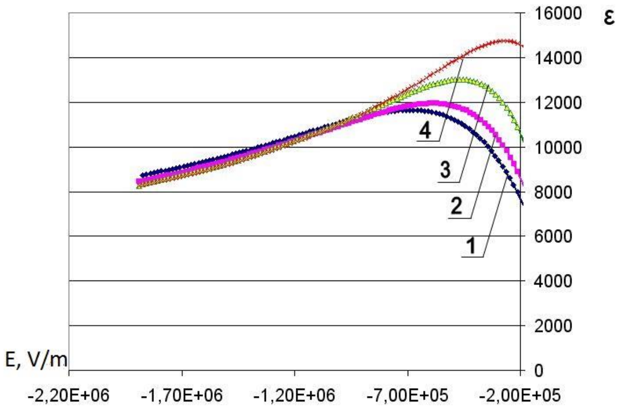

Fig. 4 – Dependence of the dielectric permittivity on the electric field strength (sample $Ba_{0,75}Sr_{0,25}Ti_{0,95}Zr_{0,05}O_3$). 1 – 24 °C; 2 – 35 °C; 3 – 55 °C; 4 – 45 °C

The biggest ferroelectric materials electrical properties nonlinearity is near the Curie point. For convenience of practical usage of the developed ferroelectric materials in high-voltage devices, the point of their phase transition should be in the range 40-50 °C, i.e. at the temperature exceeding the ambient temperature for most climatic zones. So investigations of experimental ferroelectric ceramics samples were carried out at temperatures 20-70 °C.

As can be seen from the dependencies shown in Fig. 4, these samples have the biggest nonlinearity at the temperature of 45 °C. This provides usage of such materials in high-voltage pulsed devices. Experimental data shown in Fig. 2, correspond to nanostructured ferroelectric ceramics, made from raw components grinding at liquid nitrogen temperature up to granules with submicron sizes and subsequent high-temperature synthesis with a reduced time of sintering. This enables submicron sizes of the ferroelectric ceramics domains and as a result, a short time of change of its permittivity.

Analysis of the experimental data obtained by the described method proves a possibility of creating ferroelectric ceramic with rather large nonlinearity of electrical physical properties and high polarization rate. It was shown by the carried experiments also that such a ceramic is able to withstand high voltage application without electrical breakdown. Further development of nanostructured ferroelectric materials suitable for creating of forming lines with nanosecond rise time durations requires improvement technology of their synthesis and correction of their structure by doping of ferroceramic with zirconium, lead and other elements.

To determine most suitable dielectric parameters of synthesized ferroelectric ceramics, it is expedient to use mathematical modeling of the electromagnetic processes that occur at electromagnetic waves propagation along a FL. Methods for performing such calculations are described elsewhere [8-10]. Numerical simulations [11] have shown that increase in 1.4 times of the difference in the ferroelectric non-linear dielectric permittivity causes decrease of the front duration in 3.2 times at an electromagnetic wave propagation along a FL.

CONCLUSIONS

1. Measured electrical physical properties of nanostructured barium-strontium titanates based ferroelectrics (electric displacement, dielectric permittivity, differential dielectric permittivity) as a function of the applied pulsed power electric field strength at different temperatures and velocity of voltage increase have shown expediency of usage of raw components grinding at liquid nitrogen temperature and reduced time of high-temperature synthesis for obtaining materials with large nonlinearity, high polarization rate and required electrical strength.
2. Registration of the dynamic electrical physical characteristics of nanostructured ferroelectric ceramics, which can be used as a working medium for generators of shock electromagnetic waves, was provided by the developed modernized experimental setup, based on Sawyer-Tower method and usage of Blumlein line as a source of a monotonically increasing voltage.

Електрофізичні властивості наноструктурованих сегнетоелектриків в потужних імпульсних електричних полях

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Описано експериментальні дослідження електрофізичних властивостей наноструктурованих сегнетоелектриків на основі титанату барію-стронцію в імпульсних потужних електричних полях. Розроблений стенд для проведення таких досліджень, що передбачає прикладення імпульсів напруги з субмікросекундними інтервалами фронтів та амплітудами до 20 кВ до зразків сегнетокераміки. Цей стенд дозволяє підтримувати задану температуру зразків у діапазоні від кімнатної температури до температури 70 °C. З проведених досліджень випливає, що наноструктуровані зразки, отримані шляхом спікання дрібнозернистих титанатів стронцію-барію, легованих цирконієвими порошками, розміром до десятків нанометрів, показують більші значення ступеня нелінійності діелектричної проникності при імпульсній поляризації, ніж ті, що зроблені з порошків з переважною кількістю частинок розміром більше мікронів.

Ключові слова: Нанорозмірні порошки, Сегнетоелектрична кераміка, Діелектрична проникність, Нелінійні параметри.

Электрофизические свойства наноструктурированных сегнетоэлектриков в мощных импульсных электрических полях

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Описаны экспериментальные исследования электрофизических свойств наноструктурированных сегнетоелектрикив на основе титаната бария-стронция в импульсных мощных электрических полях. Разработан стенд для проведения таких исследований, предусматривающий приложение импульсов напряжения с субмикросекундными длительностями фронтов и амплитудами до 20 кВ к образцам сегнетокерамики. Этот стенд позволяет поддерживать заданную температуру образцов в диапазоне от комнатной температуры до 70 °C. Из проведенных исследований следует, что наноструктурированные образцы, полученные путем спекания мелкозернистых титанатов стронция-бария, легированных циркониевыми порошками, размером до десятков нанометров, показывают большие значения степени нелинейности диэлектрической проницаемости при импульсной поляризации, чем те, что получены из порошков с подавляющим количеством частиц размером более микрон.

Ключевые слова: Наноразмерные порошки, Сегнетоэлектрическая керамика, Диэлектрическая проницаемость, Нелинейные характеристики.

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