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Methodology for studying polarization noise in ferroelectric materials and its application to barium titanate

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The paper proposes a method for studying polarization noise in ferroelectrics and tests it using a single crystal and ceramics of barium titanate. Polarization noise is detected, the spectral density of which is inversely proportional to the frequency of the measuring field. Polarization noise is observed only in the ferroelectric phase and correlates with the magnitude of the pyroelectric current, which indicates its connection with spontaneous polarization..

Keywords: polarization noise, ferroelectric, spontaneous polarization, phase transition, pyroelectric current.

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Introduction

Currently, there are various methods for studying the properties of ferroelectric materials. At the same time, the problem of improving these methods in order to increase their accuracy and efficiency remains pivotal. A number of methods are used to detect spontaneous polarization in ferroelectrics, such as pyroelectric response analysis, study of hysteresis loops, as well as nonlinear dielectric spectroscopy [3,4]. The application of these research methods involves applying large electric fields to the samples. However, there are a number of ferroelectric materials for which the application of high voltages is unacceptable due to their significant conductivity or possibility of electrical breakdown. Detection of polarization noises resulting from fluctuations in spontaneous polarization allows to remove these limitations. There are a number of works on the study of ferroelectrics by method of thermal noise. In some of them, the noise generator is a resistor, and the sample is a load [5,6], and there is a part of the work where the intrinsic noise of the sample [7–10] is investigated, which allows us to obtain more information about ferroelectrics. In addition, the results of the study of intrinsic thermal noise may be of practical importance [11].

When a long-range order exists in a physical system, thermal excitations tend to disrupt it. This situation is observed in ferroelectrics, where thermal fluctuations in the polar phase lead to a change in polarization $\mathbf{P}(r, t)$ and generate a noise current of polarization ($j = dP/dt$). This phenomenon is described by the well-known fluctuation-dissipation theorem [12], which delineates a general relationship between the response of a given system to external fields and spontaneous fluctuations in the absence of external perturbations. The spectral power density of thermal noise $S(\omega) = dI^2/d\omega$ for the short-circuit current generated by the polarization fluctuation has the form [13]:

$$S_I(\omega) = 4kT\omega C''(\omega), \tag{1}$$

where k — Boltzmann constant, and T — temperature, $C = C' - iC''$ — value of a capacitor filled with a material with dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$. Power can only be dissipated by the resistive component of the current, which is in the same phase with the voltage. Thus, the polarization noise is Johnson–Nyquist noise [14,15].

As follows from equation (1), the spectral power density of the current generated by polarization is proportional to the imaginary part of permittivity $\varepsilon''(\omega)$. This value usually peaks near the characteristic relaxation or resonant frequency of the system, where power dissipation is at its maximum. If we consider the frequency dependence of the dielectric permittivity $\varepsilon^*(T, \omega)$ of a ferroelectric, then it has several regions of dispersion:

$$\varepsilon^*(T, \omega)=\varepsilon_1^*(T\omega)+\varepsilon_2^*(T, \omega) + \varepsilon_3^*(T, \omega)+\varepsilon_4^(T, \omega)+ \dots, \tag{2}$$

where $\varepsilon_1(T, \omega)$ — contribution to dielectric permittivity due to a change in the value of P_s (reorientation of domains and movement of domain walls), $\varepsilon_2(T, \omega)$ — due to defects and impurities, $\varepsilon_3(T, \omega)$ — due to elastic ionic and $\varepsilon_4(T, \omega)$ — orientation polarization, which determine the Curie–Weiss law. Each of the contributions has its own temperature and frequency dependences. All of these contributions, except for elastic ion polarization, have a relaxation character and are described by Debye-like dispersion:

$$\varepsilon = \varepsilon(\infty) + \frac{\Delta\varepsilon}{1 + i\tau\omega},$$

where τ — relaxation time, and $\Delta\varepsilon$ —dielectric permittivity contribution of the appropriate polarization mechanism. Direct calculation shows that the spectral density of electric current caused by polarization fluctuations through a short-circuited capacitor filled with ferroelectric makes [10]:

$$S(\omega) = \frac{d\rangle I^2\rangle}{d\nu} = 4kTC_0\frac{\Delta\varepsilon}{\tau}\frac{(\tau\omega)^2}{1+(\tau\omega)^2},$$

where C_0 — geometrical capacity ($C_0 = \varepsilon_0 s/d$), s — area, d — thickness of sample.

In the ferroelectric phase, low-frequency noises caused by fluctuations in spontaneous polarization, movement of domain walls, and Barkhausen jumps have long relaxation times and are distributed over a certain interval. The noise induced by these processes can be observed in the low-frequency band. An analysis of the temperature dependences of these noises can make it possible to estimate the magnitude of spontaneous polarization, as well as the nature of its dependence on temperature.

In this paper, a study is conducted on the possibility of diagnosing the polar state of ferroelectrics based on the analysis of their polarization noise. As an example, samples of a single crystal of barium titanate and ceramics obtained from nanopowders with a particle size of 200 nm and sintered at different temperatures are studied.

1. Experimental setup and research technique

Low frequency noise detection system is shown in Fig. 1 The furnace for heating the sample was shielded, and was powered by direct current to reduce external noise. A ready-made AD620 instrument amplifier module was used for the preamp, with some modifications (Fig. 2). Instead of stepless gain control, discrete switching was provided (R_1, R_2, R_3) and selective feedback was added (C_1, C_2, C_3), so that the amplifier can act as a low-pass filter. The bandwidth of the amplifier without feedback is within $0-10^5$ Hz. To reduce external interference, the amplifier was powered by a separate rechargeable battery. All detecting circuit has a second shielding loop.

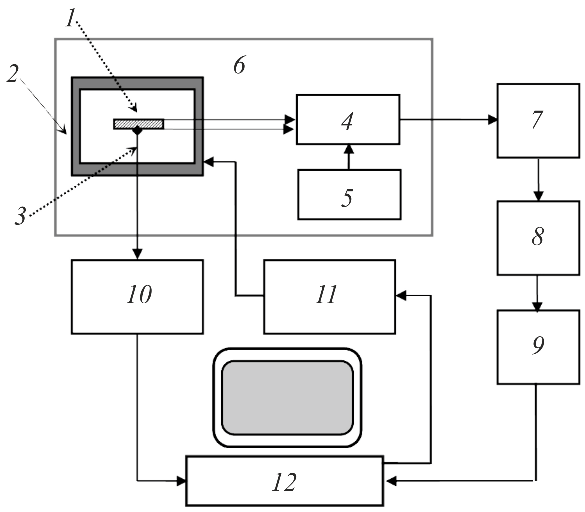

Figure 1. Measuring system: *1* — studied sample, *2* shielded heated cell, *3* — thermocouple, *4* — preamp, *5* — 5 V battery cell to supply power to the preamp, *6* — measuring system screen, *7* — controllable bandpass filter, *8* — electronic voltmeter B3-48, *9* — ADC ZET 210, *10* — electronic thermometer TC-6621, *11* — programmable power supply GW Instek GPD-4303S, *12* — personal computer.

After pre-amplification, the noise signal of the test sample was fed through a bandpass filter to an electronic millivoltmeter V3-48. 15-band equalizer (EQ215P-20181101) with the frequency band from 35 Hz to 20 kHz was used as a controllable bandpass filter. The frequency characteristics for the first four filters are shown in Fig. 3. From V3-48 output the signal through ADC ZET 210 was transmitted to the PC. The software analyzed the temperature of the sample and maintained a constant heating and cooling rate using a programmable power supply GW Instek GPD-4303S. An example of the frequency characteristics of a detecting path when several filters and a feedback circuit is shown in Fig. 4. As follows from the graph, the choice of filters and a feedback capacitor allows you to change the frequency range and bandwidth of the detecting path.

The temperature dependences of the complex dielectric constant (ε^*) were obtained using E7-25 LCR meter. In this experiment, silver paste was used as a material for making electrodes. To measure the temperature with an accuracy of $0.1\,^\circ$C the electronic thermometer TC-6621 was used. The experiments were carried out in a cyclic heating and cooling mode controlled by an automated computer-controlled system with a temperature change rate of $2\,^\circ$C per minute in the range of $30\,^\circ\mathrm{C}-160\,^\circ\mathrm{C}$.

The pyroelectric response was studied to evaluate the spontaneous polarization of the samples. If the total resistance of the sample changes during the temperature change, the most successful is to measure the pyroelectric current under short-circuit conditions (i.e., the electric field is maintained constant E) [16]. In our case, the short circuit condition was maintained using AD620 operational amplifier. The preamp was used in direct current mode without filters and the signal was sent directly to the computer via ADC ZET 210. To measure the pyroelectric current, the samples were pre-polarized at room temperature and an electric field strength of 5000 V/cm, the heating rate during measurement was kept constant and was 5 K/min.

To test the technique, a well-researched barium titanate was selected, which is a classic multiaxial ferroelectric, the spontaneous polarization of which has several possible directions. At temperatures higher than $T_\circ = 120\,^\circ$C the crystalline structure of $BaTiO_3$ — cubic with a spatial group $Pm3m$. When $BaTiO_3$ is cooled to $120\,^\circ$C, a structural phase transition occurs into tetragonal polar symmetry of class $P4mm$, stable up to temperature $5\,^\circ$C. Below the phase transition at $120\,^\circ$C a spontaneous polarization P_s with a magnitude of $18\,\mu\mathrm{C/cm^2}$ occurs in a step like manner, and when it is cooled down to the room temperature it rises to

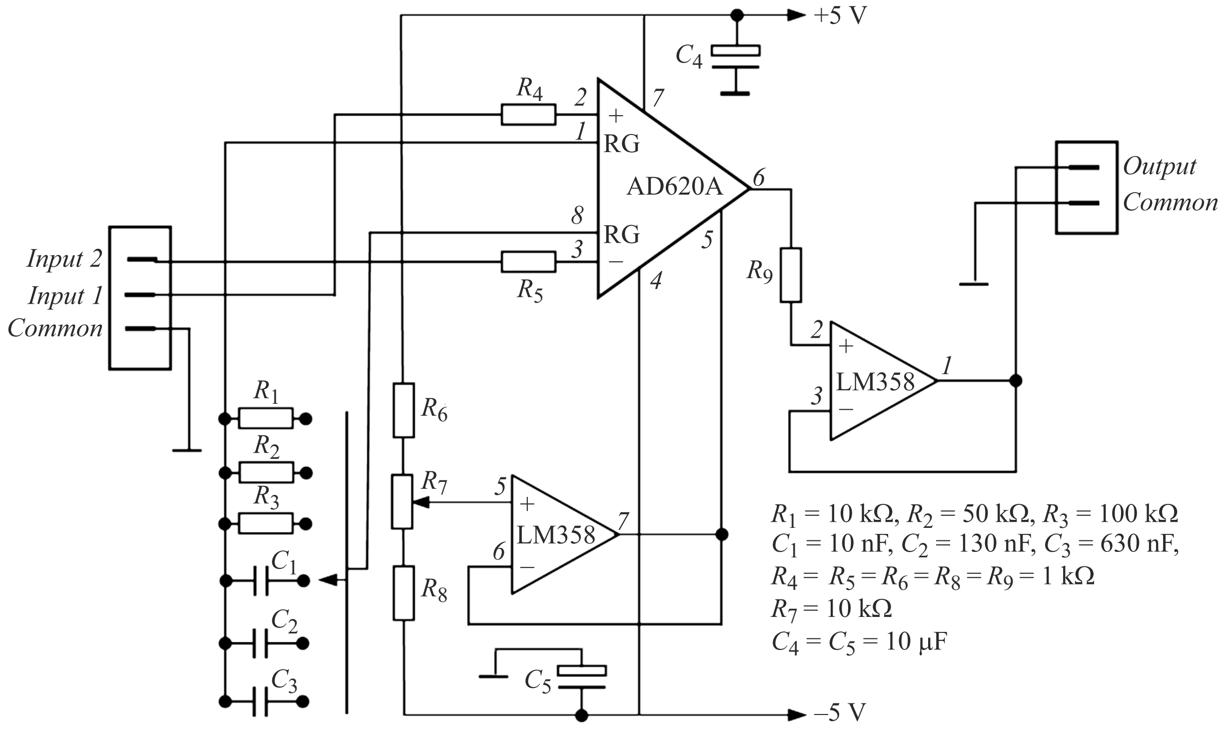

Figure 2. Preamp schematic diagram.

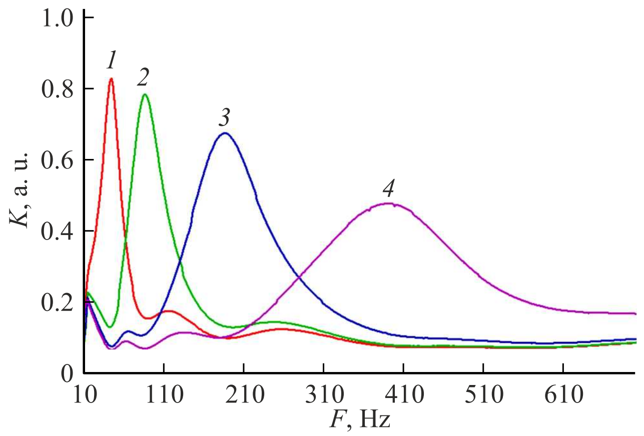

Figure 3. Transmittance coefficient K of equalizer versus frequency for the filters: *1* — 35 Hz, *2* — 75 Hz, *3* — 160 Hz and *4* — 400 Hz.

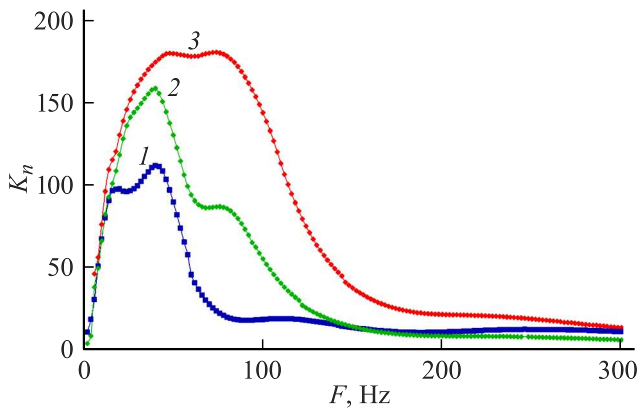

Figure 4. Detecting path gain coefficient versus frequency for different combination of filters and feedback capacitor: *1* — filter 35 Hz and $C_3 = 630$ nF, *2* — filters 35 Hz, 75 Hz and $C_2 = 130$ nF, *3* — filters 35 Hz, 75 Hz and $C_1 = 10$ nF.

about 26 μC/cm^2. At temperatures below 5 °C the crystal is transformed into a rhombic shape [1].

To fabricate $BaTiO_3$ ceramics the nanopowders made by Mann Grain Nano Technology Co., Ltd. (PRC) with a 99.9% purity were used. Average size of particles of the nano-powders was 200 nm. The workpieces were pressed at 500 kg/cm^2. Polyvinyl alcohol was used as a plasticizer. After pressing, the samples were 10 mm in diameter and 1.5 mm in thickness. Sintering was carried out with holding at temperatures of 1100 °C, 1250 °C and 1350 °C during 2 h [17].

2. Studied samples and experimental results

Fig. 5 shows the frequency dependence of noise intensity for the barium titanate ceramics sintered at a temperature of 1250 °C. As follows from the graphs, the intensity of thermal noise in the ferroelectric phase significantly depends on the frequency and decreases not at the phase transition point (123 °C), but in a certain temperature range above the phase transition.

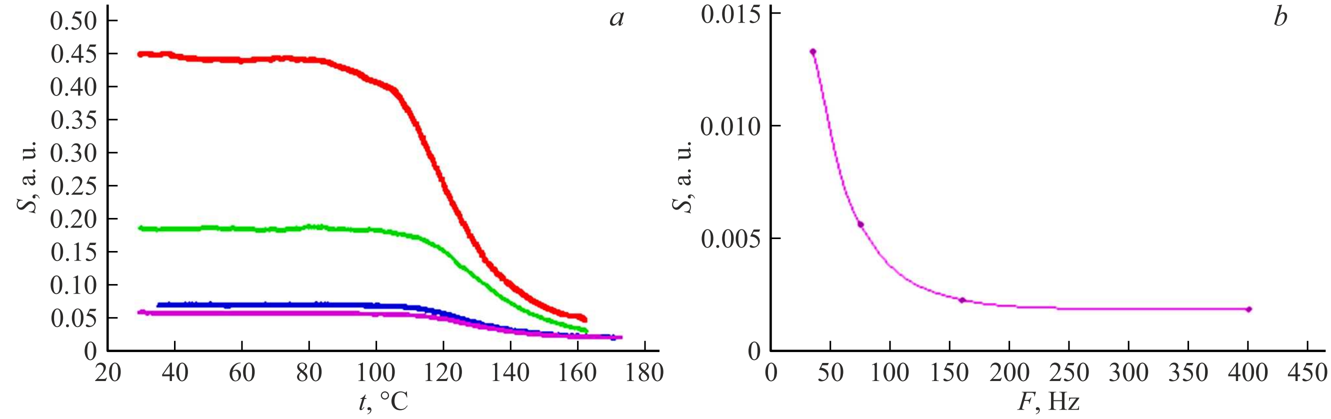

Figure 5. Noise intensity versus: temperature for the bandpass filter center frequencies 35 Hz (*1*), 75 Hz (*2*), 160 Hz (*3*) and 400 Hz (*4*), obtained for barium titanate ceramics sintered at a temperature of 1250 °C (*a*); frequency at a temperature of 40 °C, obtained for barium titanate ceramics sintered at a temperature of 1250 °C (*b*).

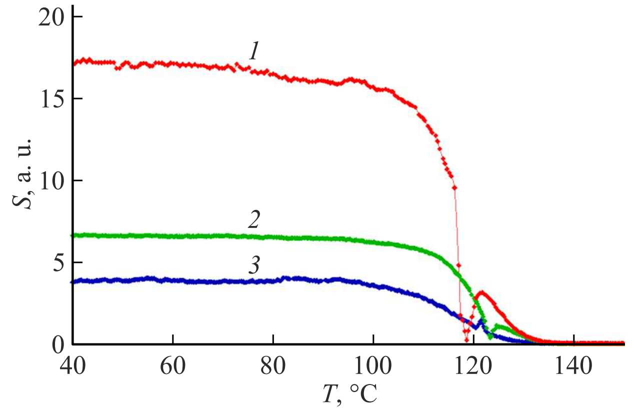

Figure 6. Dependences $S(T)$ for barium titanate samples obtained by cooling BaTiO single crystal$_3$ grown using the Remeika method (*1*), ceramics sintered at a temperature of 1350 °C (*2*), and ceramics sintered at a temperature of 1100 °C (*3*).

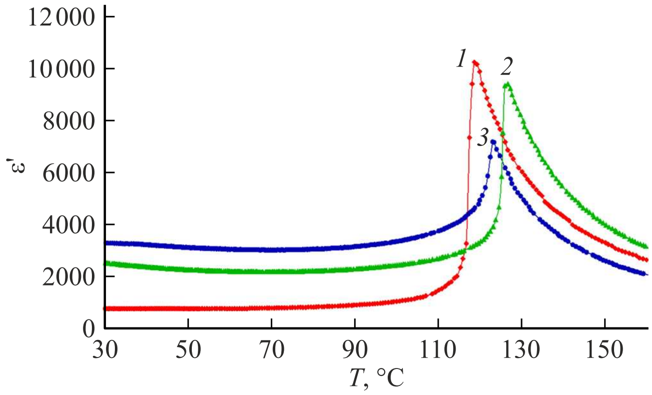

Figure 7. Temperature dependencies of dielectric permittivity $\varepsilon'(T)$ for single crystal of $BaTiO_3$ (*1*), ceramics sintered at a temperature of 1350 °C (*2*), and ceramics sintered at a temperature of 1100 °C (*3*).

When selecting the frequency range of noise detection 10–100 Hz (curve *2* in Fig. 4) on curves $S(T)$, an anomaly appears at the phase transition point due to a jump in spontaneous polarization (Fig. 6). The single crystal of barium titanate has the highest noise density (curve *1*), ceramics sintered at a temperature of 1350 °C (curve *2*) has lower noise density, and ceramics sintered at a temperature of 1100 °C has even more lower value (curve *3*).

Figure 7 shows the temperature dependences of the dielectric permittivity $\varepsilon'(T)$ at a frequency of 10 kHz for a single crystal of $BaTiO_3$ and ceramics sintered at different temperatures. For a single crystal, the maximum value of the dielectric constant at the phase transition point is 10,000, and for ceramics sintered at 1350 °C and 1100 °C — 9,000 and 7,000, respectively. The tangent of the dielectric losses of the studied samples has the same order, and for a single crystal it varies from 0.01 at room temperature to 0.025 during the phase transition, and for ceramic samples it varies from 0.015 to 0.03.

If we analyze the pyroelectric current near the phase transition for the same samples, a similar dependence is observed for it — the highest value for a single crystal and its lower value for ceramics (Fig. 8).

The obtained results of the study of polarization noise in ferroelectric materials allow us to estimate the magnitude and temperature variation in spontaneous polarization. This method is applicable in cases where large electric fields cannot be applied to the test sample. However, the method has a qualitative character, since the result may be influenced by other parameters of the samples, for example, such as the heterogeneity of the material, the presence of impurities or the conductivity of the samples.

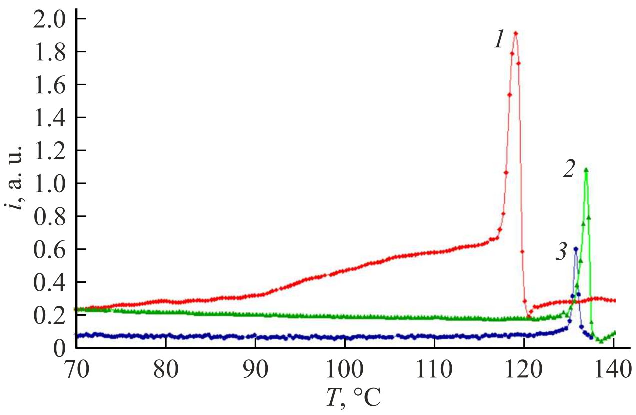

Figure 8. Temperature dependencies of pyroelectric current $i(T)$ for the single crystal of $BaTiO_3$ (*1*), ceramics sintered at a temperature of 1350 °C (*2*), and ceramics sintered at a temperature of 1100 °C (*3*).

Conclusion

Thus, in single crystals and ceramics of barium titanate, in the temperature range 30 °C–140 °C, polarization noise was detected, the spectral density of which is inversely proportional to the frequency of the measuring field f, i.e., noise of $1/f$ type. Polarization noise is observed only in the ferroelectric phase and correlates with the pyroelectric current at the temperature of the phase transition, which suggests that it is associated with spontaneous polarization and qualitatively repeats its dependence on temperature.

Conflict of interest

The authors declare that they have no conflict of interest.

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