Experimental researches of phase transitions in ceramics on the basis of barium-strontium-titanate

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***Abstract* – Application of piezoelectric crystals in acoustics demands special attention as for their nonlinear properties. It is necessary to consider piezoelectric nonlinearity and electrostriction of these crystals besides elastic nonlinearity. Nonlinear acoustic effects in piezoelectric crystals are very interesting, in particular at temperature close to temperature of phase transition. In a vicinity of phase transition the crystal lattice is labile, strong anharmonicity of phonon – phonon and photon – phonon interactions have been observed. In some solid state and liquid substances at certain external influences the phase transformations take place without change of a physical state. Thus, on the basis of described method and with various samples piezoelectric ceramics it is possible to investigate the acoustic anisotropy formed by rotating electric field at the temperatures below the 50°C.**

***Keywords* – electric field, acoustic waves, polarization, ultrasound, piezoelectric, phase transition, ferroelectric, capacity, temperature of Curie.**

I. INTRODUCTION

In previous publications [1]–[4] there has been shown the possibility of inducing of spiral and rotating acoustic structure in isotropic media, in which there is a strong dependence of permittivity on deformation. The advantages of the use of a rotating electric field have been specified on a centrosymmetric ferroelectric ceramics as an example. Of great interest is the study of the rotating acoustic anisotropy development not only in anisotropic ferroelectric ceramics but also in crystals of different classes of symmetry, as the majority of acousto - electronic devices are made with the use of a wide class of monocrystals.

When the crystal is in the electric field with amplitude E0 and components

$$E_1 = E_0 \cos\Omega t,\ E_2 = E_0 \sin\Omega t,\ E_3 = 0 \qquad (1)$$

rotating at frequency Ω round axis Z (basic vector c), there can be crystal acoustic properties change. Such field can be created, for example, by giving of electric potential with phase shift on the system of the parallel metal electrodes located on a surface of a crystal [1], [4]. Thus phase shift is defined by the number of electrodes and is equal $\pi/2$ for the case presented in figure 1.

An acoustic property of a crystal with abnormal high permittivity (for example, centrosymmetric ferroelectric ceramics based on barium titanate) is possible to describe with Hooke's law [5] taking into account viscosity of medium:

$$\sigma_{ik} = c_{iklm}\gamma_{lm} + \eta_{iklm}\frac{\partial\gamma_{lm}}{\partial t}. \qquad (2)$$

Here σ_{ik}, γ_{lm}, c_{iklm} are tensor of pressure, deformations and elastic constants; η_{iklm} is tensor of viscosity.

The influence of rotating electric field can lead to essential change of crystal acoustic properties therefore distribution of an elastic wave with a displacement vector u will be described by the motion equation:

$$\rho\frac{\partial^2\mathbf{u}_i}{\partial t^2} = \Lambda(t)\frac{\partial^2\mathbf{u}_i}{\partial z^2} + B(t)\frac{\partial}{\partial t}\frac{\partial^2\mathbf{u}_i}{\partial z^2}. \qquad (3)$$

Here ρ is density of medium, tensors of elastic constants $\Lambda(t)$ and viscosity $B(t)$ consider non - stationary influence of external rotating electric field and have the following form:

$$\Lambda(t) = U(t)\begin{pmatrix}\overline{\Lambda}+\delta & 0\\ 0 & \overline{\Lambda}-\delta\end{pmatrix}\tilde{U}(t), \qquad (4)$$

$$B(t) = U(t)\begin{pmatrix}\overline{B}+\chi & 0\\ 0 & \overline{B}-\chi\end{pmatrix}\tilde{U}(t). \qquad (5)$$

$$\mathrm{U(t)} = \begin{pmatrix}\cos\Omega t & -\sin\Omega t & 0\\ \sin\Omega t & \cos\Omega t & 0\\ 0 & 0 & 1\end{pmatrix} = \exp(\Omega t c^{x})$$ is matrix of turn round axis Z on angle Ωt [6].

In expressions (4) and (5) designations are used:

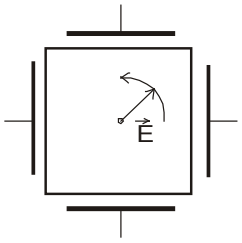

Fig. 1. The method of creation of rotating electric field.

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$$\begin{aligned}
&\bar{\Lambda} = c_{44} + (\alpha_{155} + \alpha_{144})E_0^{\,2}/2;\\
&\bar{B} = \eta_{44} + (\beta_{155} + \beta_{144})E_0^{\,2}/2;\\
&\delta = (\alpha_{155} + \alpha_{144})E_0^{\,2}/2;\\
&\chi = (\beta_{155} + \beta_{144})E_0^{\,2}/2.
\end{aligned} \tag{6}$$

α and β are tensors, considering electrostriction influence of field E on elastic constants and viscosity of medium: $\Delta\Lambda_{ijkl} = \alpha_{mnijkl}E_mE_n$, $\Delta B_{ijkl} = \beta_{mnijkl}E_mE_n$.

Similarly to [7], [1], the solution of the motion equation (3) is possible to be presented in the form of the flat monochromatic waves connected among themselves

$$\begin{aligned}
&\mathbf{u} = \{\mathbf{A}_+\mathbf{n}_+ \exp[-i(\omega-\Omega)t] +\\
&+\mathbf{A}_-\mathbf{n}_- \exp[-i(\omega+\Omega)t]\}\exp[ik(\omega)z]
\end{aligned}, \tag{7}$$

with equal wave numbers k(ω) and the different frequencies ω±Ω having opposite circular polarization. Acoustic waves in a crystal with rotating structure (7) essentially depend on the ω value, defined by frequency and polarization of the incident acoustic wave.

Let's consider a case when on a crystal boundary the circularly polarized ultrasonic wave is exited:

$$\mathbf{u}_\mathbf{e} = u_0\mathbf{n}_- \exp[-i\omega_0 t]. \tag{8}$$

Vector of elastic displacement of this wave has the same direction of rotation with time as an external electric field. As a result of continuity of elastic displacement vector on a crystal boundary the incident wave firstly generates in a crystal component of the wave with the same polarization and the frequency, described as the second composed the formulas (7). Thus $\omega_0 = \omega + \Omega$, and the crystal eigen mode can be given in the form:

$$\begin{aligned}
&\mathbf{u} = \{\mathbf{A}_-\mathbf{n}_- \exp[-i\omega_0 t] +\\
&+\mathbf{A}_+\mathbf{n}_+ \exp[-i(\omega_0 - 2\Omega)t]\}\exp[ik(\omega_0 - \Omega)z]
\end{aligned}. \tag{9}$$

The greatest interest is presented by the case $\omega_0=\Omega$, when the incident wave coincides with external electric field not only with a rotation direction, but also with frequency.

Then

$$\begin{aligned}
&\mathbf{u} = \{\mathbf{A}_-\mathbf{n}_- \exp[-i\omega_0 t] +\\
&+\mathbf{A}_+\mathbf{n}_+ \exp[i\Omega t]\}\exp[ik(0)z]
\end{aligned}, \tag{10}$$

and crystal eigen mode consists of two connected among themselves circularly polarized waves propagating in opposite directions and having identical frequencies. As polarization is defined depending on a direction of propagation of a wave, the circular components of the wave of a crystal have actually equal polarization. If frequency of an incident wave ω_0 slightly differs from the frequency of a rotating electric field the Ω so connected waves (9) have opposite directions of propagation, identical polarizations and close frequencies ω_0 and 2Ω-ω_0.

If ultrasound frequency considerably differs from the frequency of a rotating electric field, resonant interaction is not observed. In this case the incident wave (8), exits in a crystal usually one circularly polarized wave, characterized by a vector of polarization $\mathbf{n}_-$ and wave number $k_2(\omega_0-\Omega)$. In this frequency range the turn of polarization plane of ultrasound in a crystal is possible when a linearly polarized wave is exited at it [4].

If frequency of ultrasound is true to inequality $4\Omega^2 << \delta^2\omega_0^2$, then crystal eigen acoustic mode of a (7) also represents by itself two circularly polarized waves with the factor of coupling close to unit [1,4]. However in this case the energy transformation of electric field into energy of ultrasound does not occur. Hence, reversed generation and amplification of transmitted waves don't take place. At such non resonant interaction the condition is ω>>Ω, and the coupled waves propagate in a crystal in one direction that leads to simultaneous transformation of frequency and ultrasound polarization. At a certain thickness of a crystal the exited on boundary circularly polarized wave will be transformed at an exit from a crystal to a wave with opposite polarization and frequency $\omega_0\pm2\Omega$ [4].

Application of piezoelectric crystals in acoustics demands special attention to their nonlinear properties. In these crystals it is necessary to consider piezoelectric nonlinearity and electrostriction besides elastic nonlinearity. Nonlinear acoustic effects in ferroelectric crystals, especially near to temperature of phase transition are extremely interesting. In a vicinity of phase transition the crystal lattice is labile, strong anharmonicity of a phonon – phonon and a photon – phonon interactions is observed.

In some solid and liquid substances phase transformations without changing the aggregate state take place.

Transitions: ferroelectric material – paraelectric, dielectric – metal, a paramagnetic – ferromagnetic can serve as an example of phase transformations. In vicinities of phase transformations the substance structure appears extremely sensitive to external influences: thermal, electric, magnetic or mechanical, and even small changes of their sizes, near to phase transition, cause considerable changes of electric, optical, structural and other properties of substances. Phase transitions in a number of dielectrics and semiconductors are accompanied by essential reorganization of their electronic, phonon, dipole and magnon subsystems. In crystals such reorganization is connected with the change of their symmetry in vicinities phase transition.

Researches of nonlinear interaction of spatial acoustic waves and rotating electric field carried out by us [8]–[10] are related with a number of difficulties, among which are – phase transitions in a ferroelectric material. So, for example, widely used in acoustics and electronics barium titanate is in centrosymmetric condition (class m3m) at temperature above Curie temperature. If its temperature is below the temperature of phase transition, crystal structure corresponds to class 4mm with tetragonal symmetry [11].

In practice the temperature dependence of permittivity is described by the Curie – Weiss law for a ferroelectric material with phase transition:

$$\varepsilon = C/(T - T_c), \tag{11}$$

where C is constant of Curie–Weiss depending on type of a ferroelectric material; T_c is hardware temperature of Curie-Weiss at which there is a phase transition.

The most typical representative of a ferroelectric material with a phase transition of the first type is barium titanate ($BaTiO_3$). Usually it exists in the form of a fine grained polycrystalline ceramics by sintering at the temperature 1300–1400°C barium carbonate $BaCO_3$ and dioxide titan TiO_2: $BaCO_3+TiO_2 \rightarrow BaTiO_3+CO_2 \uparrow$.

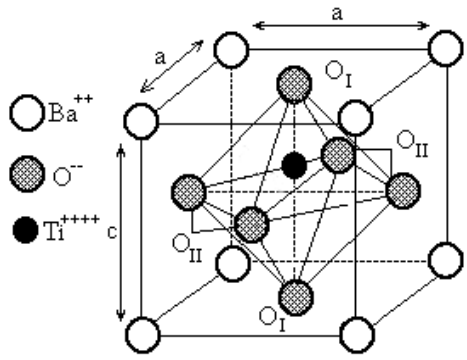

Fig. 2. Crystal structure $BaTiO_3$ at normal temperature.

Barium titanate at normal temperature has polycrystalline structure in which atoms of oxygen form an octahedron in the center of which there is an atom of the titan. Displacement of ions Ti, O_I and O_{II} accordingly on 0.014c, -0.023c, and -0.04c (fig. 2), is at the bottom of occurrence of spontaneous polarization Ps≈0.25 of C/m^2. It is necessary to note that each structural transition is accompanied by phase transition at temperature of Curie T'_c= 400° C. For pure $BaTiO_3$ hardware temperature T_c is 12° lower. Constant of Curie – Weiss for barium titanate $C=1.2\cdot10^5$ K, and $\varepsilon_{max} = 10^5$ [12-17].

Rather high temperature of Curie does not allow to investigate the property of phase transformations under usual conditions. The problem is related with the location of the sensors and the current-carrying structures. Therefore of special practical interest are ferroelectric materials with temperature of phase transition in the range of normal temperatures. Their use allows carrying out researches, without resorting to strong overheating of ferroelectric ceramics and all elements of control over the experiment.

We carried out researches of phase transition of ceramics on a basis of barium titanate with addition of strontium titanate: $BaTiO_3$ (75%) + $SrTiO_3$ (25%). The ceramics is produced by a sintering method at temperature 1200–1300°C at Institute of Solid State Physics and Semiconductors of National Academy of Sciences of Belarus (Scientific and Practical Materials Research Centre of the National Academy of Sciences of Belarus) by the group of Dr. A.I. Akimov. Such structure has allowed to lower considerably temperature of phase transition up to T_c=43°C.

In figure 3 the sample of ferroelectric of squared shape and size 10×10×50 mm is shown. On the verge of the sample conducting electrodes from copper in length of 40 mm are put. Measurement of ferroelectric parameters was made by means of definition the sample capacity placed between pairs-parallel facings.

In Figure 4 the thermostatically element of experimental setup executed from dielectric ceramics with a heating element in the form of a spiral is presented. The thermostat allows to fix the necessary temperature by means of current regulation through a heating element of the device. In the thermostat the investigated sample of ferroelectric and temperature sensor are located.

Phase transitions in ferroelectric were studied by means of the measurement of the permittivity of medium with constant geometrical parameters. Measurements were done by an indirect method. On the sample the AC voltage with the frequency 1 kHz was applied and reactance between facings was measured. The measuring device LC – meter displayed the measured capacity. Using the formula for calculation of capacity of the flat capacitor, it is possible to calculate permittivity of the investigated ferroelectric sample:

$$\varepsilon = \frac{1}{\varepsilon_0}\frac{d}{S}C, \qquad (12)$$

where S is the area of spending facings, d is distance between facings. At constant parameters d and S directly measured capacity is a function only permittivity of medium (ε). Experimental results of the measurement of ferroelectric permittivity depending on temperature are given in figure 5.

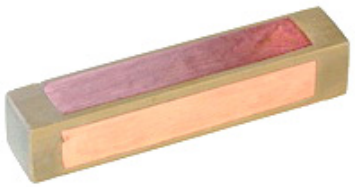

Fig. 3. The sample of ferroelectric with the conducting electrodes.

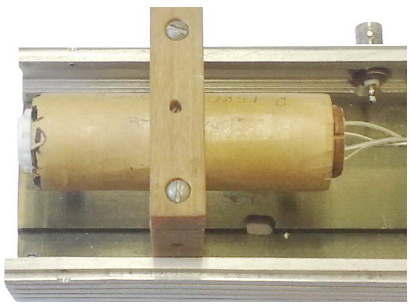

Fig. 4. Thermostatically casing with the ferroelectric sample placed in it.

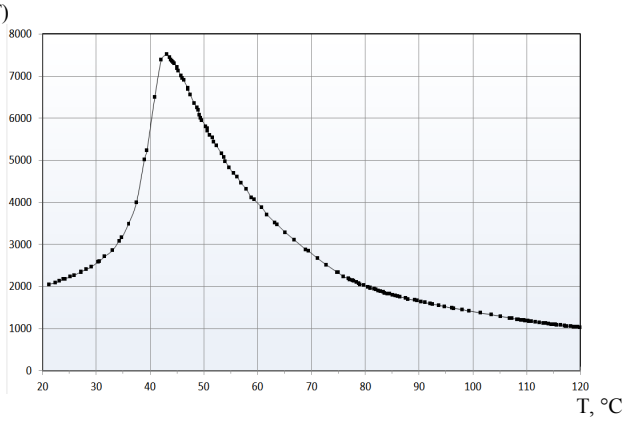

Fig. 5. Temperature dependence of permittivity.

From the schedule it is seen that high value of permittivity is achieved at temperature 43°C. That is more than twice more low for temperature of phase transition of pure barium titanate [11]. It is necessary to note that phase transition in investigated by us ferroelectric has the diffuse nature. At heating of the investigated sample to temperature of Curie the growth of permittivity has been observed. Above temperature of Curie permittivity smoothly decreases. The reason of it is spontaneous orientation of separate domains of structure of a ferroelectric material.

Thus, on the basis of the method described above and with various samples of ferroelectric ceramics it is possible to investigate the acoustic anisotropy formed by a rotating electric field at rather low temperatures, lower than 50° C.

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