

Controlling the polarization of ferroelectrics to obtain additional energy

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Abstract: - A small-size installation created using ferroelectric ceramics for generating additional electric power is considered. The use of an electrochemical generator in the plant improves the efficiency of power generation by controlling the polarization of ferroelectric ceramics and applying innovation. At consumption of 1 joule of electricity (due to mechanical energy), 2...4 joules of electricity are generated at the output. The technology of energy increase is realized in two stages: at the first stage the degree of polarization of the ferroelectric element is increased, and at the second stage the electric power supplied to the load is increased. The efficiency of the electrical installation is about 55...60% and depends on the modification of ceramics and electrical circuitry.

Keywords: - Reorientation, segnetoelectrics, solid solutions, domains, charging, polarization, energy, batteries, electric transport

Received: July 18, 2022. Revised: October 13, 2023. Accepted: November 11, 2023. Published: December 11, 2023.

1 Introduction

Studies of two-component systems of piezoceramic materials based on lead zirconate titanate (CTS) have led to the development of two-, three-, four-, and five-component systems [1].

Such high-performance materials possess segmentoelectric properties and elevated Curie temperatures (T_c). Four-component systems of complex lead-containing piezoceramic materials are widely used in industry, which have significantly higher electrophysical and mechanical characteristics (Fig. 1) compared to the two-component CTC system. However, despite the significantly improved characteristics, these multicomponent materials (segnet ceramics) are unfortunately still not used for additional energy generation. They are used (as well as previously developed CTS systems) in energy conversion devices: piezotransformers, piezosensors, piezofilters, piezomodulators, etc.

Probably, the existing idea about inexpediency of using CTS systems for obtaining additional energy due to their low electrophysical and mechanical characteristics is automatically (subconsciously) "transferred" to these more efficient materials.

2 Factors determining the control of polarization in obtaining additional energy

One of the main features of materials with piezo effect is a rigid temperature interval in which their piezoactive properties are manifested. The upper point of this interval is the Curie temperature T_k . Segnetoelectric perovskites exhibit polymorphism depending on temperature, that is, their cube-shaped cell is distorted in various ways. Basically 3 forms or phases are used: tetragonal (T), rhombic and rhombohedral (Re), Figure 2. The boundaries between these temperatures are called phase transitions [2, 3]. These boundaries are "blurred" for many physical characteristics. As established [1], for four-component systems of solid solutions, the "blurring" in concentration transitions between tetragonal and rhombohedral phases is 2-5% of the change in titanium concentration along a certain section with promising material properties for it. This "blur" is denoted as the morphological region (MO). The reorientation polarization P_r (the number of domain reorientations remaining after removal of the electric field at preliminary polarization of the segnetoelectric) is important when selecting a segnetoelectric [1], just as K_p is the mechanical activity. The excess energy is achieved by controlling the polarization of the segnetoelectric,

which is determined by the choice of operating temperature range and frequency range and basically boils down to the following:
 -choice of segnetoelectric material and circuitry for its inclusion in an electrical circuit;
 -Selection of the frequency range and operating temperature range.

Figure 1 shows the K_p , P_r , d_{31} , g_{31} and ϵ/ϵ_0 curves. The figure shows that for the temperature interval corresponding to the rhombohedral segmented phase, the values of K_p , P_r , d_{31} , g_{31} , and ϵ/ϵ_0 are practically stable. P_r , d_{31} , K_p , and g_{31} significantly decrease in the transition to the tetragonal phase. ϵ/ϵ_0 is minimal, which corresponds to an increase in K_p , and increases during the transition to the tetragonal phase. It follows from the graphs that the maximum electromechanical activity of the K_p and the piezoelectric coefficient d_{31} depend on the residual polarization P_r and the relative permittivity ϵ/ϵ_0 .

These parameters of the crystals of the same name are in dependence, (1).

$$K_p = 2 \sqrt{\frac{2}{1-\sigma}} \sqrt{\frac{\epsilon_{33}^T}{S_{11}^E}} \cdot Q_{12} \cdot P_r, \quad (1)$$

where Q_{12} is the coefficient of electrostriction, σ and S_{11}^E are Poisson's and pliability coefficients, respectively, ϵ_{33}^T -dielectric permittivity.

Q is the Poisson's ratio and is a reference value. In calculations of devices using piezo- and segnetoelectrics, as a rule, $\sigma = 0.24 - 0.4$ depending on the chemical composition.

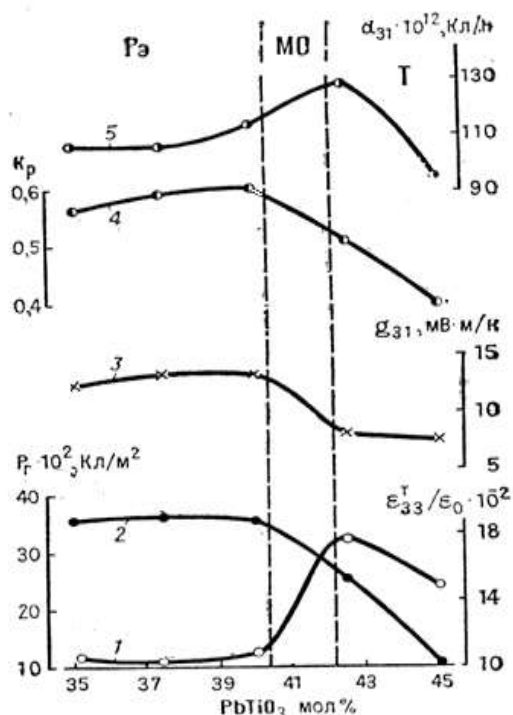


Figure 1. Composition dependences $\epsilon_{33}^T/\epsilon_0$ (1), P_r (2), g_{31} (3), K_p (4), and d_{31} (5) for the system $PbTiO_3 - PbZrO_3 - PbNb_{2/3}Mg_{1/3}O_3 - PbNb_{2/3}Ni_{1/3}O_3$.

Thus, the mechanical activity of K_p is sensitive to P_r and its maximum is in the rhombohedral region, which is defined for the crystals of the same name by a certain temperature interval near MO, i.e., the interval of operating temperatures t_p . The MO can be analyzed, for example, by means of concentration-temperature (C-T) phase diagrams, Figure 2 [1].

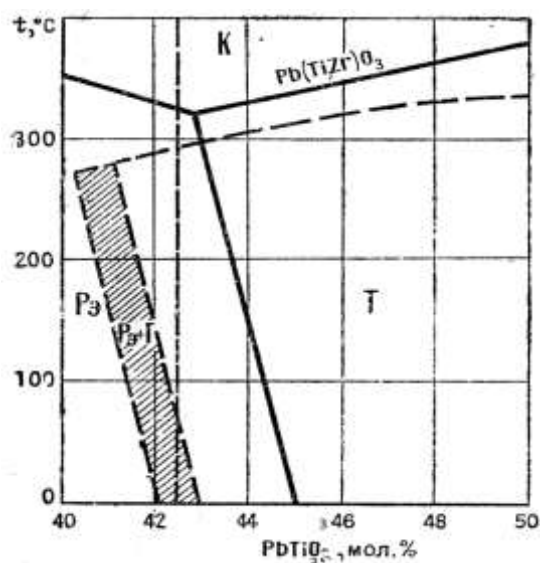


Figure 2. Phase diagram (C-T) of the system $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbNb}_{2/3}\text{Ni}_{1/3}\text{O}_3 - \text{PbK}_{1/2}\text{Mn}_{1/2}\text{O}_3$ (dashed lines). The solid lines correspond to the CTS system

The figure shows the slope of the MO toward the rhombohedral phase for a four-component system of the form [1]: $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{Pb} B'_{1-\alpha} B'' O_3 - \text{Pb} B'''_{1-\beta} B'''' O_3$, где $\alpha(\beta) = 1/2, 1/3, 1/4$ depending on the valence of the cations B', B'', B''', B'''' .

The cations that provide segnetoelectric properties can be the chemical elements Sb, Li, Bi and others of a certain valence.

The slope is determined by the concentration of the titanium-containing compound PbTiO_3 in a given solid solution of the four-component system. And the concentration of PbTiO_3 in solution is correlated with the phase transition temperature.

Thus, for example, 41% of PbTiO_3 corresponds to approximately 110°C of the segnetoelectric. The composition of the rhombohedral phase near the MO, as the temperature increases, transitions through the MO to the tetragonal T phase and then to the cubic K (paraelectric cubic) phase. This is explained by the fact that at large (critical) concentrations of titaniumTi near the MO, its atoms tend to stably shift. Therefore, the whole system tends to move to the tetragonal phase through the MO. As a result, the shape and volume of the cell change.

It was found [1] that the maximum number of residual 71° - degree domain reorientations of P_r is in the rhombohedral phase. The orientation is determined in the direction perpendicular to the sample surface. It is known that the values of maximum reorientation polarization P_r and residual P_r are part of the spontaneous polarization of the P_s domains and are determined by the sum of all domain rotations and the polarization process. As a result of studies the degrees of domain reorientations under the action of electric field and residual, after removal of the field were determined.

It was also found [1] that the fraction of 71° - degree maximal (and also residual) reorientations in the rhombohedral phase with respect to P_s is approximately 86% ($P_r \approx 0.866$). Figure 3(b) shows domains of P_s oriented spontaneously (less than 20%) and domains of P_r oriented at approximately 71° angles to the crystal surface (over 80%).

As mentioned above, the reorientation domains in the rhombohedral segnetophase are oriented at an angle of 71° . In addition, the piezoelectric moduli in segnetoelectrics, which characterize changes in electric polarization under the action of mechanical

loads, reach large values in the phase transition region (rhombohedral), increasing K_p , Figure 1. 71° -degree domains under the action of mechanical loads, reducing the angle, reduce the residual deformation, Figure 3, and strengthen the local electric field inside the dielectric E_1 , lining up along it.

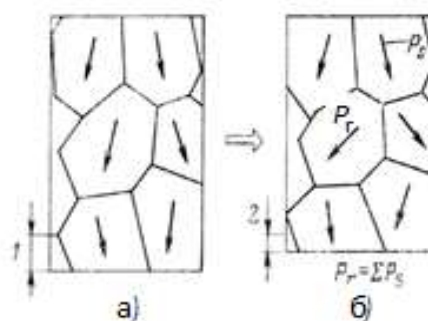


Figure 3. Ceramic polarization process. a - electric field is applied; b - after removal of electric field; 1 - electrostriction [3] deformation ; 2 - residual deformation; P_s - spontaneous (spontaneous) polarization [3]; P_r - oriented polarization.

Thus, the electric energy of the segnetoelectric increases W : $W = -\mu_d \cdot E_1 \cdot \cos Q$ [3], where μ_d is the dipole moment, Q is an angle equal to approximately 71° , figure 4.

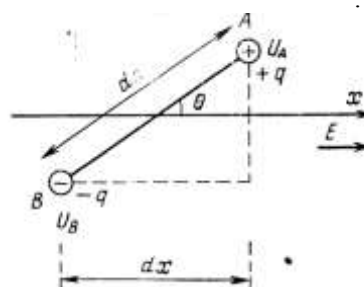


Figure 4. To calculate the domain energy possessed by the dipole moment

q - charges; U_a and U_b - charge potentials, d_s - distance between charges.

The energy of segnetoelectric domains W is directly related to its polarization P . Whereas, polarization is equal to the average value of electric moments of dipoles μ_d located in one cubic meter of segnetoelectric and is equal to the surface density of polarization charges q , i.e., $P = q/A$, where A is the surface area of the segnetoelectric.

The local electric field in a segnetoelectric induced by charges generated under the action of mechanical loads can be significant and exceed the external electric field.

The increase in the local electric field E_1 is also promoted by another piezoelectric modulus g_{31} , figure 1. The maximum g_{31} is shifted to the rhombohedral region and characterizes the tension E_1 arising under the action of mechanical stresses T , in accordance with the dependence $E \approx -g \cdot T$ [3].

Thus, by varying the concentration of the titanium-containing compound $PbTiO_3$ in the system of solid solutions of multicomponent segnetoelectrics, it is possible to control the t_p of devices based on them and to reach the maximum value of K_p .

Assume that a ferroelectric ceramic plate serves as an electromechanical transducer and creates compression oscillations along its length, Figure 5. To create a mathematical model it is necessary to develop the equation of motion of the transducer, to select the equations of the piezoelectric effect, and to make basic assumptions. The basic assumptions are as follows:
 - all mechanical stresses, except those in the direction of the transducer, are zero;
 - the amplitude of alternating mechanical stresses and strains does not exceed the maximum limiting values;
 - the change in the reactive component of the transducer impedance at operating frequencies has a capacitive character.

Let us determine the frequency constants of the transducer by solving the differential equations of piezoelectric oscillations for the assumptions defined above.

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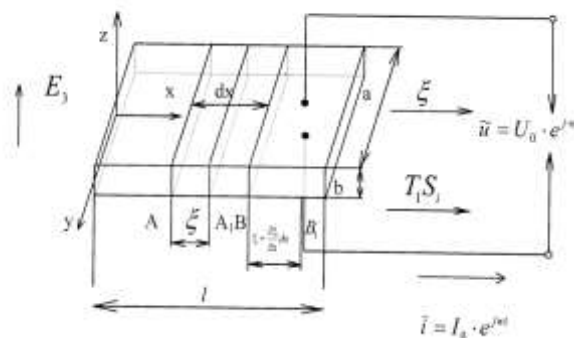


Figure 5. Diagram of the electromechanical transducer in interaction with ECG.

The equation of motion of the transducer is:

$$\frac{\partial^2 \cdot \xi}{\partial \cdot x} = \frac{1}{v^2} \cdot \frac{\partial^2 \cdot \xi}{\partial \cdot t^2}, \quad (2)$$

where ξ is amplitude of oscillation (displacement);

$v = \sqrt{\gamma / \rho}$ - speed of elastic wave propagation in the plate;

γ - modulus of elasticity of ferro piezoelectric ceramics;

ρ - ferro piezoelectric ceramics density;

l, a and b - length, width and thickness of the plate, respectively;

t - time.

This is a well- studied partial differential equation of second order.

The equation of motion of the transducer is solved by variable separation method:

$$\xi(x, t) = X(x) \cdot T(t),$$

$$\frac{1}{X(x)} \cdot \frac{\partial^2 x}{\partial x^2} = \frac{1}{v^2} \cdot \frac{1}{T(t)} \cdot \frac{\partial^2 T}{\partial t^2} = -n^2 \quad (3)$$

The solutions are the following, respectively:

$$X = A \cdot \cos nx + B \cdot \sin nx,$$

$$T = C \cdot \cos nvt + D \sin nvt = M \cdot \cos(nvt + \varphi),$$

where $n = m \cdot \pi / l$ ($m = 1, 2, 3 \dots$). (4)

The resonance and antiresonance oscillation frequencies of the ferro-piezoelectric plate are determined for a fixed transducer. The boundary conditions are written as follows:

$$\xi(x, t) = X(0) \cdot T(t) = 0$$

$$\xi(x, t) = X(l) \cdot T(t) = 0, \quad (5)$$

where l is the length of the plate. Omitting the intermediate calculations given in [4, 5], we give the expressions for f_r and f_a , (6).

$$f_r = \frac{1}{4l} \cdot \sqrt{\frac{Y_{11}}{\rho}} \text{ kHz}, f_a = f_r \left(\frac{K_c^2}{2.46} + 1 \right) = \frac{1}{4l} \left(\frac{K_c^2}{2.46} + 1 \right) \cdot \sqrt{Y_{11}/\rho}, \text{ kHz} \quad (6)$$

Thus, resonant and antiresonant frequencies can be approximated, which is important for calculating power plant specifications.

If an alternating electric voltage is applied to a segmented dielectric, the polarization does not follow the electric field, which leads to dielectric losses. When a mechanical load is applied, the deformation is established with a delay. That is, these processes correspond to a phase shift. All materials are subject to relaxation processes to a greater or lesser degree. Relaxation processes in ferroelectrics appear due to mechanical and dielectric losses. The peculiarities of ferroelectricity of ferroelectrics operating in the dynamic mode is the presence of both types of losses. At low frequencies, the angles of dielectric and mechanical losses in it make a total loss angle δ , defined through K_c [3-7], see equation (7). Therefore, the polarization is considered as a complex number: $\epsilon_{rk} = \epsilon_r - j \epsilon_r'$, where ϵ_r is relative dielectric constant; ϵ_r' - imaginary part of the complex number, loss coefficient ($\epsilon_r' = \text{tg}\delta \cdot \epsilon_r$); $\text{tg}\delta$ - loss characteristic; δ - phase shift angle.

The frequency characteristics ϵ_r , ϵ_r' and δ depending on the normalized frequency ω/ω_0 are as shown in figure 6.

Now it is possible to explain ECG operation principle in more detail. Under mechanical load, as a result of the clamping of ferroelectric, there is a sharp decrease in ϵ_r , Figure 6, which leads to electrical capacity reduction and an increase in K_c , that is, to a sharp increase in the efficiency of conversion of mechanical energy into electrical energy. In a certain frequency range between the resonance and the antiresonance, where the deformation will increase sharply to a greater extent than is due to mechanical load, a sudden absorption of mechanical energy occurs. This leads to a sharp increase in the degree of polarization.

Reducing the electrical capacitance of the ferroelectric ECG leads to an increase in the electrical voltage U_0 , see equation (8), and, therefore, an increase in the electrical power in the load EU . Phase transitions in ferroelectrics occur within certain temperature ranges. In this connection,

it should be noted that in ferroelectrics some piezoelectric moduli, characterizing the change in the degree of polarization under mechanical loading, reach very large values during phase transitions, theoretically passing into infinity. Thus, the effect of mechanical load in a certain frequency range and the effect of thermal energy in a certain temperature range are a sort of a catalyst of chemical reactions in solid solutions of ferroelectrics and mainly increase the specific power and specific energy of the ECG.

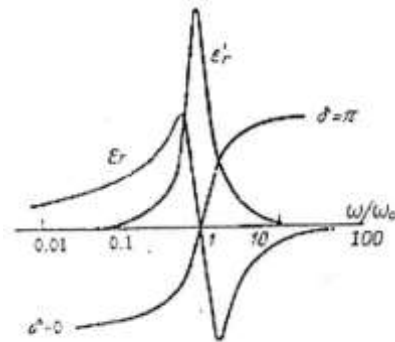


Figure 6. To the analysis of ECG resonance parameters.

The absolute dielectric constants, ϵ_α^S of the clamped element in this case are, of course, less than ϵ_α^T of the free one and are linked by equation of electromechanical coupling:

$$\epsilon_a^S = \epsilon_a^T \left(1 - \frac{d^2}{S^E \epsilon_a^T} \right) = \epsilon_a^T \left(1 - Kc^2 \right) \quad (7),$$

where Kc is electromechanical coupling coefficient, S^E is elastic compliance while the electric field strength is $E=0$, ϵ_α^T is absolute dielectric constants where the mechanical stress is $T=0$ and d is piezoelectric module [3-5].

In the general case, the transformation function (ECG) is of the form: expression (8).

From equation (7) it is obvious that the value of Kc has a significant effect on the ratio of dielectric constant of clamped and free ferroelectrics, i. e. change in the dielectric constant under the action of mechanical load. For example, in case of $Kc = 0.5$ (an averaged value), this ratio will be 0.75. Which, in its turn, is highly important (especially since in modern ferroelectric ceramics $Kc = 0.6...0.7$ for output electricvoltage (output power) of the power plant, see equation (8), as dielectric constant and electrical capacity are directly proportional.

$$U_0 = K_u \frac{d_{ij} \cdot F}{C_{ECG} + C_L}, \quad (8)$$

where U_0 means output electric voltage of ECG, F is acting mechanical force, C_{ECG} is electrical capacity of ECG, C_L is electrical load capacity (load electrical devices), K_u is coefficient of electric voltage increase due to the increased degree of polarization of ferroelectric and d_{ij} is piezoelectric module, induced polarization per unit of mechanical stress.

3 Applying technology to generate additional energy

In the future, a large amount of additional electricity and networks of chargers and charging stations will be required to charge electric vehicles. To address this problem, a power supply unit (EU), Figure 7, was developed for slow, fast, and accelerated battery charging, which is a battery charger and charging station using polarization control of segnetoelectrics.

Polarization control creates a technology to reduce energy consumption by changing the compressibility and electroelasticity of segnetoelectrics [3, 7-10]. As a result, additional energy is released that is 2.5 to 3 times greater (depending on the segnetoelectric modification and inclusion in electric circuits) than the energy consumed from an alternating electric voltage source. This additional electrical energy is also the result of the second kind of segnetoelectric transition, migration and dipole polarization.

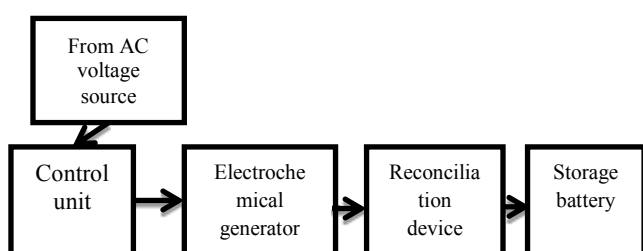


Figure 7. Functional diagram of the EU for charging.

The range of an electric car on a single charge is much less than the consumer needs. Its energy source (batteries) weighs a lot and is expensive. The reason is that the energy density of modern batteries is too low. Although the energy density of batteries has recently increased, they still weigh a lot, are large and expensive. The known simple ways to

increase the energy density of batteries have all but been exhausted. In order for batteries to replace traditionally used internal combustion engines, their energy density must be increased by a factor of about 10. The use of solar and wind energy is still inefficient. In addition, the national interests of hydrocarbon-producing countries are a deterrent to the development of electric vehicles. Thus, the problem of battery energy needs to be solved. Toyota's solid-state batteries, which promise to greatly increase energy density, are still under development. And it could be a decade or more before these batteries become mass-produced. With this in mind, an innovative small-scale alternative powertrain (EU) technology has been developed that uses an electrochemical generator (ECG) based on ferroelectric ceramics and provides a simultaneous increase in power density and specific energy. The unit also includes a mechanical energy generation unit and an electromechanical converter Figure 8. The energy consumption of 1 joule when using mechanical energy makes it possible to obtain 2.5...4 joules of electrical energy at the output. The mechanical energy used is produced by a device of simple design. The unit also includes a device for obtaining mechanical energy and electromechanical converter, Figure 8.

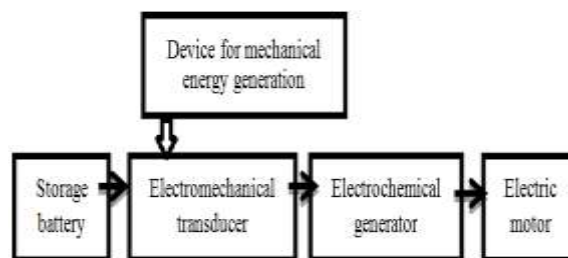


Figure 8. Functional diagram of the EU.

4 Dependence of the EU mass on the electric power it generates

Theoretical and experimental studies [5-7, 11, 12] showed that an increase in the electrical power in the load (P_L) by 2 times leads to an increase in the ECG mass (M_{ECG}) by $2\sqrt{2}$ times, by 3 times - by $3\sqrt{3}$ times and etc. In other words, these changes occur according to the law of geometric progression. And electromechanical converter and device, which

generates mechanical energy increase this mass by 2,12...2 times.

Thus, the mass of the power plant (without battery and electric motor) makes 2.12...2.2. M_{ECG} .

Figure 9 shows the growth-increase diagram of the $M_{ECG} - P_L$. The above the diagram makes it possible to calculate the mass of the EU (without the battery and electric motor) taking P_L into account. You can find a point on the diagram where $P_L = 1.89$ kW and $M_{ECG} = 0.83$ kg, near which P_L and M_{ECG} change almost directly in proportion. The M_{ECG} grows slower below this point and faster above it.

M_{ECG} , kg

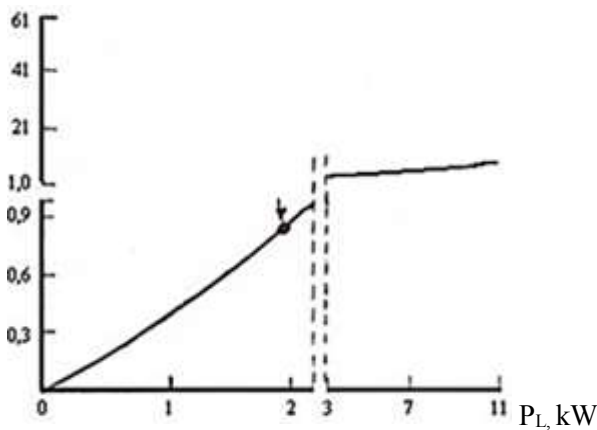


Figure 9. $M_{ECG} - P_L$ growth-increase diagram.

Figure 10 shows the character of the electrical voltage change for ECG at frequencies below resonance, where the oscillator resistance can be considered purely capacitive [5].

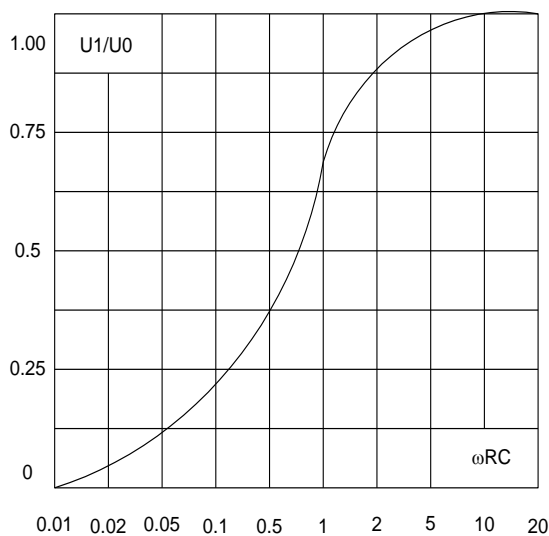


Figure 10. Frequency response of ECG.

U_0 - this is the amplitude value of the voltage that appeared on the capacitance C at $R \rightarrow \infty$.

U_1 - voltage proportional to the change in mechanical load F , (8).

The curve in Figure 10 is a part of the experimental amplitude-frequency response of the electromechanical transducer made of the ferroelectric material PZT-19, diameter 10x1 mm with a mechanical load of 2.5 MPa (see in [4], Figure 4. 1, curve 2), in the frequency range between antiresonance and resonance. Depending on the nature of the electrical load of the EU (reactive or active), the scheme of connection and consumption of electrical energy changes [4,5]

5 Conclusion

The proposed alternative innovative technology for obtaining additional energy compared to solar and wind technologies has an advantage: it does not depend on climatic conditions, time of day and has a high efficiency. The efficiency of conversion of mechanical energy into electric voltage is increased by about an order of magnitude due to the electrophysical characteristics of segnetoelectrics and physical and technical solutions (technologies). The papers [4,5] present experimental dependences of the output electric voltage on the mechanical load of segmentoelectric elements of different modification and inclusion scheme.

The increase in energy density occurs in two stages: at the first stage there is an increase in the polarization of the segnetoelectric, and at the second stage there is an increase in the electric power at the output of the EU power unit [13, 14].

Engineering-physical solutions (innovations) have been applied in the technology. Technical details of the innovations are not disclosed yet, as work is underway to improve the technology. The main components of EU are protected by copyright certificates and patents, and their performance has been confirmed by experimental studies [4,5].

Further research is aimed at studying the effectiveness of EU application for hydrogen and hybrid vehicles, as well as for increasing the energy density of batteries used for electric energy storage.

So, controlling the degree of polarization of ferroelectrics to produce additional energy is mainly determined by the following:

- The modification of ferroelectrics and the electrical connection scheme;
- mechanical loading (design features of the EU);
- interlayer or dipole polarization of ferroelectrics in the range of operating temperatures, as well as frequencies in the range of about 1...1.5 (10³ - 10⁵) Hz.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

The author contributed in the present research, at all stages from the formulation of the problem to the final findings and solution.

Sources of Funding for Research Presented in a Scientific Article or Scientific Article Itself

No funding was received for conducting this study.

Conflict of Interest

The author has no conflict of interest to declare that is relevant to the content of this article.

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