

## Tuning of piezoelectric parameters in the phase transition process via the transient state

*V.M.Ishchuk, N.A.Spiridonov* \*

Institute for Single Crystals, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine,  
60 Lenin Ave., 61001 Kharkiv, Ukraine

\*STC "Reaktivelektron", National Academy of Sciences of Ukraine,  
83096 Donetsk, Ukraine

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The influence of the electric field on the stability of phases in antiferroelectric substance with a small difference in energies of the ferroelectric (FE) and antiferroelectric (AFE) states is studied. It is theoretically predicted that the interaction between the coexisting domains of (FE) and (AFE) phases provides the stability of the inhomogeneous intermediate state of the substance in external electric field. The composition-electric field phase diagrams with intermediate state are obtained for the lanthanum modified lead zirconate-titanate based solid solutions. Variation of piezoelectric properties of these solid solutions during the phase transition via intermediate state is studied. The effective control of piezoelectric parameters is shown to be possible in materials with such phase transition.

Исследовано влияние электрического поля на устойчивость фаз в антисегнетоэлектрическом веществе с незначительной разностью энергий между сегнетоэлектрической (СЭ) и антисегнетоэлектрической (АСЭ) фазами. Теоретически предсказано, что взаимодействие между сосуществующими доменами СЭ и АСЭ фаз обеспечивает устойчивость неоднородного промежуточного состояния вещества во внешнем электрическом поле. Для модифицированных танталом твердых растворов на основе цирконата-титаната свинца получены фазовые диаграммы состава в электрическом поле. Исследованы изменения пьезоэлектрических свойств этих твердых растворов при фазовом переходе с участием промежуточного состояния. Показана возможность эффективного регулирования пьезоэлектрических параметров в материалах, которым свойственен такой фазовый переход.

The most common control method of the piezoelectric resonator frequency is based on the use of the elastoelectric effect, i.e. of the non-linear properties of piezoelectric materials.

An electric field  $E$  (DC and AC fields) applied to a piezoelectric (ferroelectric FE) element changes the dielectric, piezoelectric, and elastic constants of the substance. The state equations for the substance have the following form:

$$\begin{aligned} \eta_1 &= s_{11}^E \tau_1 + s_{111}^E \tau_1^2 + d_{31} E_3 + d_{311} E_3 \tau_1 + R_{31} E_3^2; \quad (1) \\ D_3 &= d_{31} \tau_1 + d_{311} \tau_1^2 + \epsilon_{33}^T E_3 + R_{31} E_3 \tau_1 + \epsilon_{333}^T E_3^2. \end{aligned}$$

Here the second-order effects are taken into account. In first approximation,

$$\begin{aligned} \eta_1 &= s_{11}^{\epsilon} \tau_1 + d_{31}^{\epsilon} E_3; \quad (2) \\ D_3 &= d_{31}^{\epsilon} \tau_1 + \epsilon_{33}^{\epsilon} E_3. \end{aligned}$$

In these formulas,  $d_{311}$ ,  $\epsilon_{333}$  and  $R_{31}$  are the non-linear piezoelectric, dielectric, and electrostriction coefficients, respectively. In this approximation, the effective constants of the medium depend linearly on the applied DC field strength. The analysis of the motion equations for the electric bias vector allows us to obtain the dependence of the resonance

frequency on the applied field strength [1]:

$$f_r(E_3) = f_r(0) \left[ 1 + \left( \frac{d_{32} + d_{33} - d_{31}}{2} - \frac{d_{311}}{2s_{11}^E} \right) E_3 \right]. \quad (3)$$

The slope of the field dependence of the resonance frequency is

$$\alpha_r = \left( \frac{d_{32} + d_{33} - d_{31}}{2} - \frac{d_{311}}{2s_{11}^E} \right). \quad (4)$$

The Table contains the slope values for the field dependence of the resonance frequency in some most investigated piezo- and FE crystals [1]. Such crystals make it possible to control the parameters within a very narrow frequency range. Therefore, now new physical effects are searched for which will provide a higher degree of the piezoelectric parameters controlling.

During PT via intermediate state, the fraction of the FE phase increases gradually in the bulk of the substance, whereas the other phase fraction decreases. Since antiferroelectric AFE state is piezoelectrically inactive and FE state is piezoelectrically active, at PT from AFE into FE state induced by electric field, which is realized via intermediate state, a gradual variation in piezoelectric properties of the substance could be expected.

The goal of the present work is to investigate the PT via intermediate state in lead zirconate-titanate (PZT) based solid solutions as well as the behavior of the piezoelectric properties of these solid solutions in the course of such transition.

For an infinite sample, the thermodynamic potential density of two-phase (AFE and FE) system can be presented as:

$$\varphi = \varphi_1 \cdot \xi_1 + \varphi_2 \cdot \xi_2 + W_{int}, \quad (5)$$

where  $\xi_1$  and  $\xi_2$  are the fractions of the sample volume occupied by each phase;  $W_{int}$  describes the interaction between the domains of these phases.

The phase interaction energy comprises two summands:

$$W_{1,2} = \xi_2 \cdot \sum_{i,j} [E_{\eta_{1,i}}(x_2, y_2, z_2) \cdot \eta_{2,j}(x_2, y_2, z_2)], \quad (6a)$$

$$W_{2,1} = \xi_1 \cdot \sum_{i,j} [E_{\eta_{2,j}}(x_1, y_1, z_1) \cdot \eta_{1,i}(x_1, y_1, z_1)]. \quad (6b)$$

Here  $\eta_{1,i}$  and  $\eta_{2,j}$  are the order parameters of the first and second phases, respec-

Table. The slope of the field dependence of the resonance frequency for nonlinear crystals

Crystal	Crystal cut (degrees)	$10^{-8} \alpha_r, \text{ mm/V}$
KH <sub>2</sub> PO <sub>4</sub>	45	3.0
LiJO <sub>3</sub>	0	17.4
NaNH <sub>4</sub> SeO <sub>4</sub> ·2H <sub>2</sub> O	45	14.8
	26.34	14.9
	63.26	6.22
Bi <sub>12</sub> GeO <sub>20</sub>	18.26	14.0
	71.34	4.19
	45	11.3
	26.34	18.6
Bi <sub>12</sub> SiO <sub>20</sub>	63.26	7.70
	18.26	17.57
	71.34	5.30
	45	14.0

tively ( $i$  and  $j$  being the numbers of the order parameters for these phases);  $E_{\eta_{1,i}}(x_2, y_2, z_2)$  are the fields induced in the second phase domain by nonzero values of the order parameters of the first phase domain;  $E_{\eta_{2,j}}(x_1, y_1, z_1)$  are the fields in the first phase domain induced by the nonzero values of the order parameters of the second phase domain. Based on the physical nature of the order parameters (or the coexisting phases), it is evident that not all the products included in the expressions (6a) and (6b) are nonzero. This is due to symmetry of the order parameters and fields. Only terms which are transformed according to the representations containing the identity one, are nonzero in the expressions (6a) and (6b).

We shall restrict ourselves by the approximation where Eq.(6) is expanded into a series of the powers of  $\eta_{\alpha,i}$ :

$$E_{\eta_{1,i}}(x_2, y_2, z_2) = \xi_1 \cdot C_{1,i}(x_2, y_2, z_2) \cdot \eta_{1,i} + \dots, \quad (7a)$$

$$E_{\eta_{2,j}}(x_1, y_1, z_1) = \xi_2 \cdot D_{2,j}(x_1, y_1, z_1) \cdot \eta_{2,j} + \dots \quad (7b)$$

Note that the considered fields are rather long-range fields.

In the case when external fields are present, they may be taken into account in (5) in the usual way:

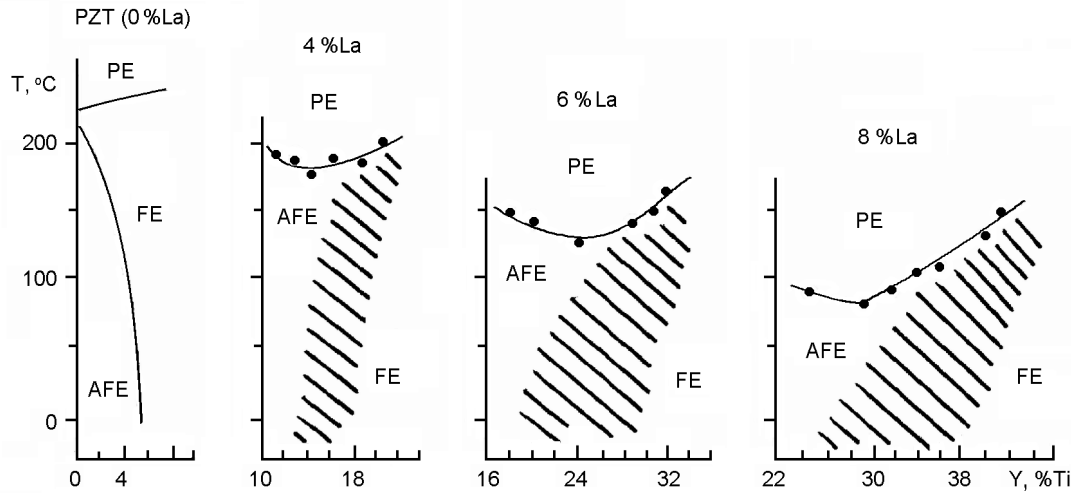


Fig. 1. Evolution of the composition-temperature phase diagram of PZT solid solutions for successive substitution of lanthanum for lead.

$$W_{ext} = -E_{\alpha,i;ext} \cdot \eta_{\alpha,i},$$

where  $E_{\alpha,i;ext}$  is the external field conjugate to the order parameter  $\eta_{\alpha,i}$ .

Thus, the behavior study of the system of interacting coexisting phase domains is reduced to the investigation of thermodynamic potential (5) with  $W_{int}$  in the form (6), taking into account the expressions (7) under the condition  $\sum_{\alpha} \xi_{\alpha} = 1$  ( $\alpha = 1;2$ ). Our

next step is the conventional minimization procedure for the nonequilibrium thermodynamic potential

$$\Phi_{\lambda} = \Phi - E_{\alpha,i;ext} \cdot \eta_{\alpha,i} - \lambda \cdot (\sum_{\alpha} \xi_{\alpha} - 1), \quad (8)$$

where  $\lambda$  is the indeterminate Lagrangian multiplier. This procedure results in a system of equations for determination of the equilibrium values of the order parameters.

$$\xi_{\alpha} \cdot (\partial\Phi_{\alpha}/\partial\eta_{\alpha,i} + E_{\eta_{\alpha,i}} - E_{\alpha,i;ext}) = 0, (\xi_{\alpha} \neq 0) \quad (9)$$

$$\Phi_{\alpha} + \eta_{\alpha,i} \cdot E_{\alpha,i;int} = \lambda = const, \quad (10)$$

$$E_{\alpha,i;int} = E_{\alpha,i;ext} - E_{\eta_{\alpha,i}}. \quad (11)$$

As is seen from Eq.(10), the condition for the coexistence of thermodynamically equilibrium multiphase structure is the equality of thermodynamic potentials of the phases, taking into account the external and internal effective fields. The fields  $E_{\eta_{\alpha,i}}$  are spatially varied. Therefore, at the same

value of the external field  $E_{\alpha,i;ext}$  AFE  $\rightarrow$  FE transition may take place only in certain local regions of the sample (but not in the whole sample). This means that, within a certain interval of the external electric field strength, the domains of the phases participating in the transition coexist in the sample bulk. By analogy with magnets or superconductors, such a state is called the intermediate state (IS) in AFE.

As was shown in [2, 3], the fraction of FE phase rises linearly in the IS range when external electric field is applied to the sample:

$$\xi_1 \cong \frac{E_{ext} - E_{pt}}{C \cdot P_{1,0}^E}. \quad (12)$$

The boundaries of IS (the electric field intensities for the onset and the end of the transition) are defined by the equations (from the conditions of  $\zeta_1 = 0$  and  $\zeta_2 = 1$ ):

$$E_1 \cong E_{pt}; \quad E_2 \cong E_{pt} + C \cdot P_{1,0}(E_{pt}). \quad (13)$$

In two last equations,  $E_{pt}$  is the electric field strength at which the AFE  $\rightarrow$  FE state PT takes place when the phase interaction is absent;  $P_{1,0}(E_{pt})$ , the FE phase polarization when the applied DC field strength equals to  $E_{pt}$  and  $C > 0$ .

Ceramic samples of the lanthanum modified  $PbZr_{1-y}Ti_yO_3$  solid solutions were obtained by joint co-precipitation from the mixed aqueous solutions of lead and lanthanum nitrates and chlorides of titanium and zirconium with subsequent two-stage synthesis at 550°C and 850°C. The polycrystalline samples were obtained by sintering at 1300–1340°C in a controlled PbO atmosphere. The resulting grain size was found to be 6 to 8  $\mu m$ .

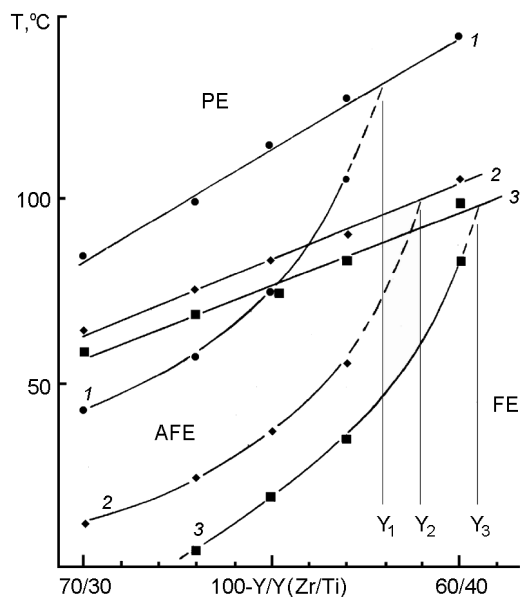


Fig. 2. Phase diagrams for X/100-Y/Y PLZT solid solutions with the content of lanthanum X (per cent): 7.50 (1), 8.25 (2), 8.75 (3).

The crystal structure of the samples was studied using a SIEMENS D-500 powder diffractometer with a Ge monochromator ( $\text{CuK}\alpha_1$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ) and a BRAUN gas position-sensitive detector. The accuracy of  $2\theta$  angle measurements was  $0.01^\circ$ . X-ray diffraction analysis confirmed that the samples were single-phase with perovskite crystal structure. The spontaneous polarization was measured with a modified Sawyer-Tower circuit at  $5 \cdot 10^{-3}$  Hz frequency. Piezoelectric measurements were

made in accordance with IEEE Standard [4], but some modification of these methods was made (as it was described in [1]) for measurements in strong external DC electric field. The samples for piezoelectric and polarization measurements were shaped as 1 mm thick disks of 12 mm in diameter.

The evolution of the "composition-temperature" phase diagram for lanthanum modified lead zirconate titanate solid solutions (PLZT) near the boundary separating the regions with the FE and AFE ordering at a successive increase of the La content [3, 5] is given in Fig. 1. According to the X-ray analysis and transmission electron microscopy data [3, 6–8], these phase diagrams include a region (shaded in Fig. 1) where the coexisting domains of the FE and AFE phases are present in the solid solutions. These regions in Fig. 1 form the hysteresis range for the AFE-FE phase transition in an external electric field.

We have investigated the conditions for the intermediate state induction by the external electric field and the behavior of the piezoelectric characteristics of materials during that induction. The PLZT solid solutions with the following compositions: 7.5/100-Y/Y, 8.25/100-Y/Y, and 8.75/100-Y/Y (where 7.5, 8.25, and 8.75 characterize the percentages of La substitution for Pb; 100-Y and Y are the percentage of Zr and Ti, respectively) were used in our experiments. Detailed phase diagrams for the solid solutions under investigation are shown in Fig. 2. The vertical lines  $Y_i$  ( $i = 1, 2, 3$ ) are the boundaries of the spontaneous FE state regions (for each series of solid solutions, respectively). For the solid solu-

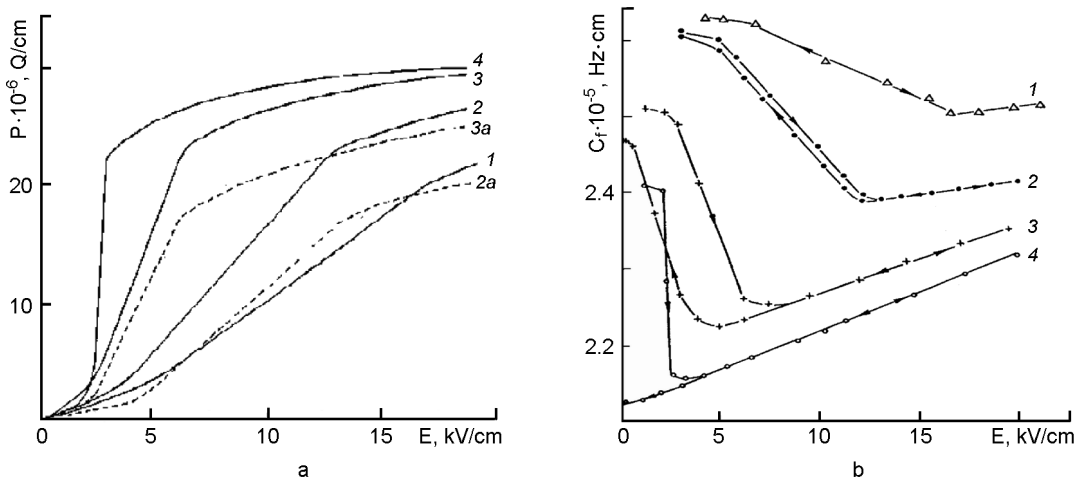


Fig. 3. Electric field dependences of polarization (a) and frequency constant (b) for PLZT with 8.25 % of lanthanum. Content of Zr/Ti: 72/28 (1), 70/30 (2), 67/33 (3), 65/35 (4).

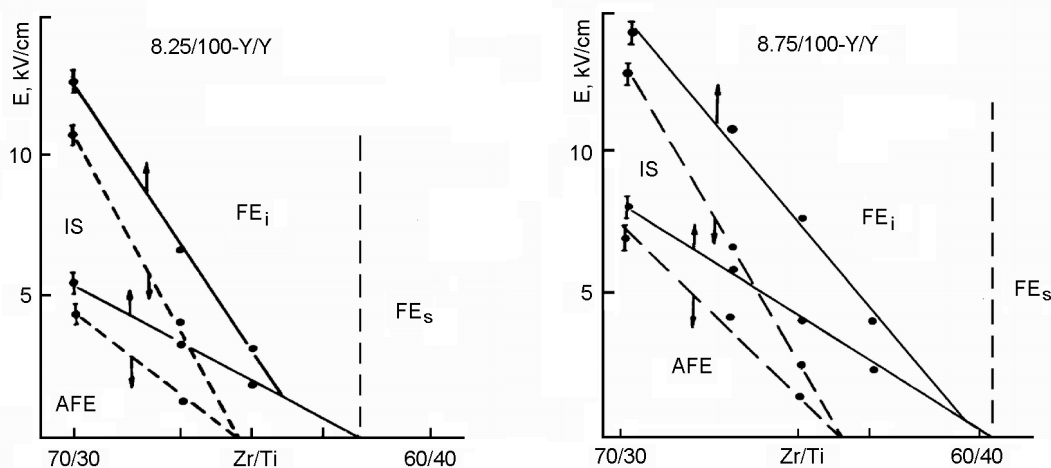


Fig. 4. Composition-electric field phase diagrams for 8.25/100-Y/Y (at the left) and 8.75/100-Y/Y (at the right) PLZT solid solutions.

tions with Ti concentrations located to the right of the vertical lines  $Y_i$ , the low-temperature ( $T < T_c$ ) phase is ferroelectric. In the solid solutions under consideration, the AFE state is more stable at lower Ti concentrations. The FE state can be induced by an external electric field in solid solutions with compositions located near the region of spontaneous FE state in the phase diagram (see Fig. 2) at low temperatures  $T < T_{0,i}(Y)$ . This induced FE state will be preserved under heating until the temperature reaches a characteristic value  $T_{0,i}(Y)$ . Since the "composition-temperature" phase diagrams for all above-mentioned series of solid solutions are physically similar, in what follows, we present the main results for the solid solutions with 8.25/100-Y/Y composition.

The electric field dependence of polarization at room temperature (20°C) is presented in the Fig. 3a (the samples were previously annealed at 600°C). The first harmonic frequency of radial oscillations was measured as a function of the DC electric field. The dependences of the frequency constant  $C_f = r \cdot f_r$  (here  $f_r$  is the frequency, and  $r$  is the sample radius) on electric field are shown in Fig. 3b. In contrast to  $P(E)$ , the dependences  $C_f(E)$  are non-monotonic, therefore, they provide a more precise determination of the critical fields of the phase transition.

As is seen from the curves 1 in Fig. 3a and 3b, there are three intervals of external electric field where the sample properties differ noticeably when the field strength increases. In the absence of electric field, this solid solution is in the AFE state and it is preserved within the field interval  $0 < E <$

$E_{cr,1} = 4.0$  kV/cm. At high fields ( $E > E_{cr,2} = 12.5$  kV/cm) the sample is in FE state. When the field intensity is in the interval from 4.0 to 12.5 kV/cm, the polarization linearly increases. This interval is the intermediate state region in the studied solid solutions. Increase of the Zr content in solid solution results in a widening of the intermediate state region.

The results of measurements discussed above allowed us to build the "composition - electric field" phase diagrams that represent the dependences  $E_{cr,1}(Y)$  and  $E_{cr,2}(Y)$ . These diagrams containing the intermediate state region are presented in Fig. 4 for 8.25/100-Y/Y and 8.75/100-Y/Y solid solutions. In this Figure, the notations IS,  $FE_i$ , and  $FE_s$  are used for the intermediate state, induced FE phase, and spontaneous FE phase, respectively. As is seen from the "composition-temperature" phase diagram in Fig. 2, the region of the AFE phase stability is shifted towards the solid solutions with higher Ti content when the La concentration increases. The intermediate state region is also shifted in the same direction when the La content increases (see Fig. 4).

The fraction of FE phase increases linearly with the increase of the external DC field in the region of intermediate state (in compliance with (12)). The increase of the polar phase fraction should result in changes of the sample piezoelectric characteristics. The experimental results confirm this conclusion. Dependences of piezoresonance parameters on electric field are presented in Fig. 5 and Fig. 6 for some solid solutions from the series 8.25/100-Y/Y. The resonance curves for 8.25/70/30 PLZT

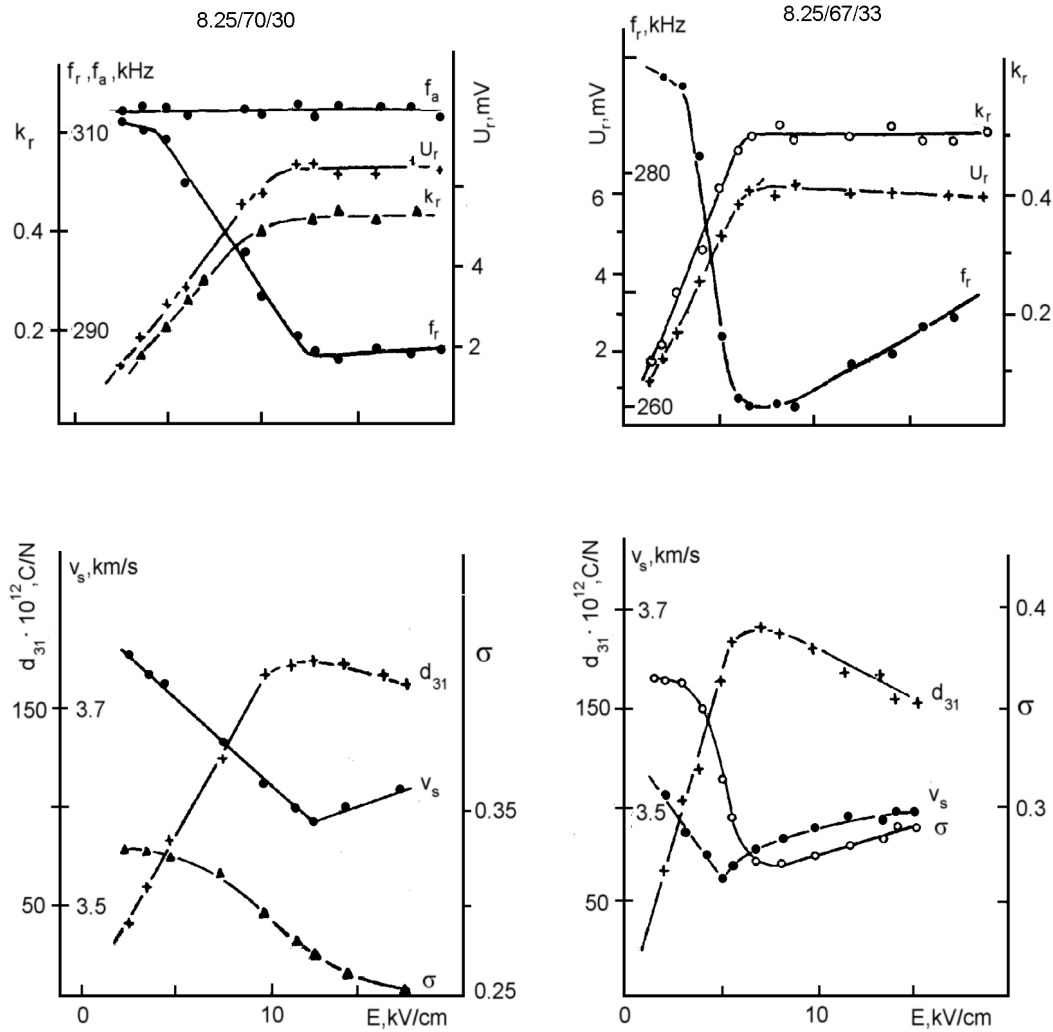


Fig. 5. Influence of external electric field on parameters of the 8.25/70/30 PLZT and 8.25/67/33 PLZT (radial resonance).

solid solution at different strengths of the external DC electric field are shown in Fig. 7 as an example.

As it follows from the phenomenological consideration [9–12], the AFE → FE phase transition has to occur in a sharp abrupt manner. However, a different behavior is observed in our experiments. The transition takes place within a finite interval of electric fields. The width of the transition increases when the solid solution composition moves away from the region of FE states in the "composition-temperature" phase diagram (Fig. 1 and 2).

The phase transition AFE → FE via intermediate state (when  $E_{cr,1} < E < E_{cr,2}$ ) occurs by means of the motion of interphase boundaries. The internal state of the AFE and FE domains remains unchanged. The polarization increase at  $E > 12.5$  kV/cm is

associated with the change of the internal state (from AFE to FE) of the preserved AFE phase domains. This process seems to be incomplete, since there is still no saturation in the curves 1a and 2a in Fig. 3, which present the sample polarization after the subtraction of  $P_i = \epsilon \cdot E$ . The AFE phase presence in the samples placed in high fields was observed in light scattering experiments [13, 14], in solid solutions with compositions belonging to the same interval of the "composition-temperature" diagram and close to those studied here. The existence conditions of these AFE domains in high electric field can be obtained from the theoretical analysis when the interaction between the AFE and FE phases is taken into account.

Let us now discuss the dependence of the intermediate state region width (the width of the interval of electric field where this

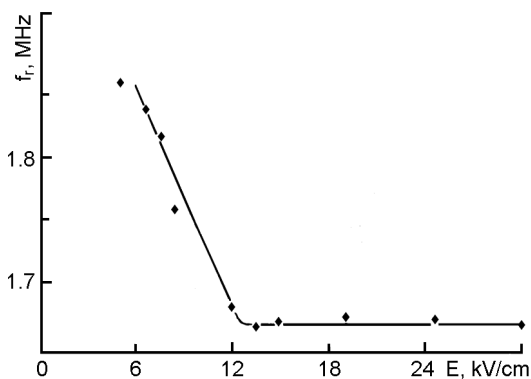


Fig. 6. Dependence of the resonance frequency (the thickness resonance) on the external electric field in 8.25/70/30 PLZT.

state is observed) on the solid solution composition. This dependence is caused by the mutual influence of the AFE and FE phase domains. It follows from (13) that the width of the intermediate state region

$$E_{end} - E_{onc} = C \cdot P_{1,0}(E_{pt})$$

is determined by the value of induced polarization inside the FE phase domain. Since the stability of the AFE state in solid solutions in question increases with increasing Zr content, the transition field  $E_{pt}$  value will also increase. As follows from [9–12], the  $P_{1,0}(E_{pt})$  value increases noticeably when the induction of the FE state field takes place at higher values of the electric field strength. This means that the  $P_{1,0}(E_{pt})$  value rises with the increasing Zr content in solid solutions under investigation. As a consequence, the interval of electric field values where the intermediate state takes place also widens with increasing Zr content.

The characteristic feature of the AFE  $\rightarrow$  FE phase transition via intermediate state is that the FE phase fraction in the sample increases in the course of the transition and as a result, the piezoelectricity of the material rises. This circumstance makes it possible to use this phase transition for effective control of piezoelectric parameters of material by external electric field (see Figs. 5 and 6). A significant change of the resonance frequency exceeding similar characteristics of known materials by several orders of magnitude has engaged out attention. It should be particularly emphasized here that this resonance frequency change is not associated with changing linear sizes of resonators in an electric field. The dependences of the sample strains on the applied

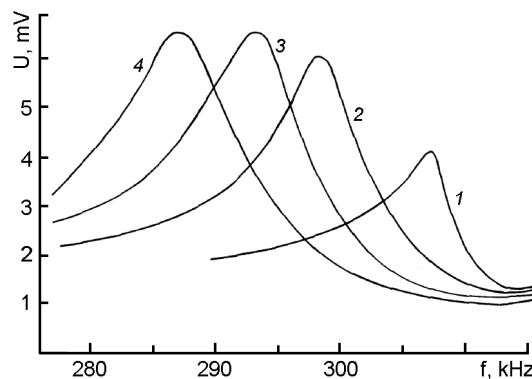


Fig. 7. Resonance curves of 8.25/70/30 PLZT at different values of external electric field.  $E$  (kV/cm): 5.0 (1), 8.0 (2), 10.0 (3), 13.0 (4).

electric field strength given in [15] for the solid solution compositions close to those studied in this work. The relative strains less than  $10^{-3}$  observed in [15] in the fields with strengths of the order of 10 kV/cm cannot be compared with the relative changes of resonance frequency observed in our experiments. Moreover, the relative strains in the direction along the applied electric field and in the perpendicular direction have different signs.

The dependence of the longitudinal resonance frequency (the thickness resonance for the geometry of our samples) on the applied field strength at the phase transition via intermediate state is given in the Fig. 6 for comparison. The sign of the effect for both longitudinal and transverse (radial) resonances is seen to be the same. These data allow us to neglect the changes of resonator linear sizes in applied electric field during the analysis of the resonator behavior in external electric field.

As indicated above, the phase transition via an intermediate state accompanied by the displacement of the interphase boundaries without changing internal state of domains of both coexisting phases ends when the fraction of the induced FE phase is close to unity. However, the complete transition to the homogeneous FE state does not take place at the electric field strengths achieved in our measurements. The AFE phase domains are still present in the sample volume (in the FE matrix). When the electric field strength is higher than the second critical value, the further increase of the field strength results in a change of the AFE internal state and the displacement of the interphase boundaries is not a major factor more. Such process causes another mechanism of resonance frequency changes. As is

seen in Fig. 3b, the sign of the resonance frequency change becomes opposite to that observed when the applied field strength values were within the range  $E_{cr,1} < E < E_{cr,2}$ . The reason for that change is that the system effective rigidity increases (due to decrease of contribution caused by the mobile interphase boundaries) when the phase state homogeneity in the system increases. The controllability of the resonance frequency becomes higher in the fields  $E > E_{cr,2}$ . The hysteresis is completely absent and the changes in the piezoelectric parameters are weak.

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## Регулювання п'єзоелектричних параметрів у процесі фазового переходу через проміжний стан

**В.М.Іщук, Н.А.Спирідонов**

Досліджено вплив електричного поля на стабільність фаз в антисегнетоелектричній речовині з незначною різницею енергій між сегнетоелектричною (СЕ) та антисегнетоелектричною (АСЕ) фазами. Теоретично передбачено, що взаємодія між співіснуючими доменами СЕ та АСЕ фаз забезпечує стабільність неоднорідного проміжного стану речовини у зовнішньому електричному полі. Для модифікованих танталом твердих розчинів на основі цирконату-титанату свинцю одержано фазові діаграми складу в електричному полі. Досліджено зміни п'єзоелектричних властивостей цих твердих розчинів при фазовому переході за участю проміжного стану. Показано можливість ефективного регулювання п'єзоелектричних параметрів у матеріалах, яким притаманний такий фазовий перехід.