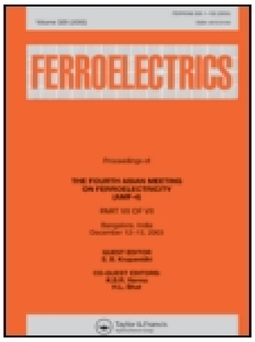

Ferroelectrics

ISSN: 0015-0193 (Print) 1563-5112 (Online) Journal homepage: http://www.tandfonline.com/loi/gfer20

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To cite this article: P. Hana , L. Burianova , S. J. Zhang , T. R. Shrout , E. Furman , V. Ryzhenko & P. Bury (2005) Elastic Stiffness Constants of PZN-4.5%PT Single Crystal Influenced by DC Bias Electric Field Applied at Various Directions to Prototypic Crystal Symmetry, Ferroelectrics, 319:1, 145-154, DOI: 10.1080/00150190590965785

To link to this article: http://dx.doi.org/10.1080/00150190590965785

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Ferroelectrics, 319:145–154, 2005
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ISSN: 0015-0193 print / 1563-5112 online
DOI: 10.1080/00150190590965785

Elastic Stiffness Constants of PZN-4.5%PT Single Crystal Influenced by DC Bias Electric Field Applied at Various Directions to Prototypic Crystal Symmetry

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The purpose of this work was to characterize an influence of the electric bias field on the elastic stiffness constants of important and unusual piezoelectric material Lead Zinc Niobate-Lead Titanate (PZN-PT). The longitudinal and transverse mode of sound propagation in single crystals containing 4.5% PT were studied. The influence of electric field, which poles the sample, is investigated by the pulse-echo sound propagation technique. From these measurements, the values of complex elastic stiffness constants are evaluated at different poling conditions with different frequencies for longitudinal and sheer excitations. Crystal cuts [001], [110] and [111] served for measurements of the elastic stiffness constants under application of the electric field. Aspects of field-induced phase transitions in PZN-4.5%PT single crystals at room temperature are discussed. Hysteretic behavior has an influence on attenuation and velocity of ultrasound.

Keywords Single crystals; longitudinal and shear waves; pulse echo overlap; phase velocity; attenuation; complex elastic stiffness constants

PACS: 77.22.Ej; 77.80.Dj

Introduction

The measurement of ultrasonic velocity, attenuation and evaluation of complex elastic stiffness of PZN: PT 4.5% single crystals are presented in this paper. PZN-PT crystals have extremely high piezoelectric coupling coefficients exceeding 90 percent. Furthermore, these samples are known to have extremely soft dielectric as well as elastic response. It is believed that a large portion of this response is due to intrinsic polarizability of these materials. Close to the morphotropic boundary, these materials permit easy rotation of polarization for samples with the electric field for the crystals in which the two are not

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Received September 6, 2004; In revised form January 31, 2005.
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parallel such as in 001 oriented rhombohedral crystals. It is useful to understand how elastic response in these crystals is modified by applied or internal electric fields since for high drive applications crystals can be utilized with the applied dc bias, which prevents depoling. Furthermore, elastic constant is important contributor to the piezoelectric coupling, and to further understand how DC bias contributes to the coupling, a study of elastic constants under bias is required. We studied behavior of the samples influenced by DC electric field bias by bulk wave pulse echo method.

At room temperature, our crystals are rhombohedral with the polarization along the ⟨111⟩ directions of the prototypic cubic parent phase. For the case of the poling direction being along [001] a multidomain structure exists at moderate fields with the tetragonal macrosymmetry. Such domain-engineered single crystals have very high electromechanical coefficient and enormous field-induced strains exceeding one percent. At higher applied fields, a true single domain tetragonal phase is induced with a single domain state becoming possible in principle.

In this article we studied effect of polarization state of PZN-PT crystals on complex elastic constants by means of ultrasonic pulse echo measurement technique. The measurements were interpreted based on the theoretical models for poled and un-poled samples [1, 2]. A single transducer method uses the same transducer to excite the traveling elastic pulse and collects attenuated reflected pulse from the same surface used for the excitation. In general returned pulse can show both pulse shape distortions due to the dispersive elastic properties as well as attenuation due to energy dissipation in the sample from both intrinsic (single domain) as well as extrinsic (defects, domain walls, intrinsic nonuniformity in relaxors, such as PZN-PT on the rhombohedral side) contributions. An example of measured ultrasonic response of a PZN-PT ⟨111⟩ crystal is shown in Fig. 1. Pulses are equally spaced in time and availability of several echoes permit high precision in estimating complex elastic constants. The basic principles of measurement phase velocity and attenuation and derivation from them of complex elastic constants are described in the paper and are applied to the observed results.

In this work we are also focused on E-field induced phase transitions of PZN-4.5% PT single crystals cuts at room temperature. The purpose of this work was to characterize an influence of the electric bias field on the elastic stiffness constants.

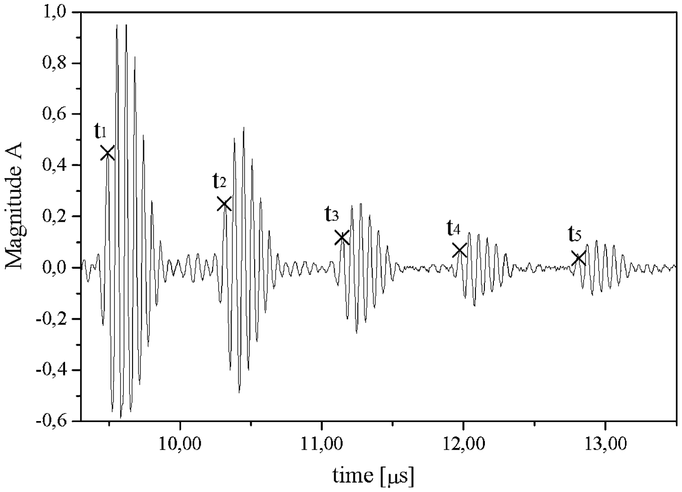

Figure 1. The response of PZN: 4.5%PT ⟨111⟩. The crosses sign the times of the flights t_i.

There are three used crystal orientations. The first one is [001], [010] and [100], the second one is [110], [$1\bar{1}0$] and [001] and the third one is [111], [$1\bar{1}0$] and [$11\bar{2}$]. The dimensions of all samples are $4 \times 4 \times 2$ mm^3. The normal axis to the largest plain is used as the first crystal orientation.

Measurement of Phase Velocity and Attenuation

The phase velocity v of the wave can be generally expressed as ratio of the thickness d of the sample and time of flight τ of the ultrasonic echoes generated by reflections at a pair of parallel surfaces of the sample. In the case of a single transducer used for sending and receiving, a linear function of times of flights is used for expressing of the averaged velocity from response spectrum in Figs. 1 and 2:

$$\mathrm{t_i} = \mathrm{t_1} + \tau \cdot \mathrm{i}, \quad \mathrm{i} = 1, 2 \ldots \mathrm{n} \quad \bar{\mathrm{v}} = \frac{2\mathrm{d}}{\tau}. \tag{1}$$

The attenuation coefficient α can be generally expressed from Fig. 3 in standard units as:

$$\alpha = -\ln \frac{\mathrm{A_{n+1}}}{\mathrm{A_n}} \Big/ 2\mathrm{d}\ [neper \cdot \mathrm{m}^{-1}] \quad \text{or} \quad \alpha' = -10 \log \frac{\mathrm{A_{n+1}}}{\mathrm{A_n}} \Big/ 2\mathrm{d}\ [\mathrm{dB} \cdot \mathrm{m}^{-1}] \tag{2}$$

We are using a linear function of logarithm of magnitude for evaluation of attenuation α:

$$\ln \mathrm{A_i} = \ln \mathrm{A_1} - \alpha \cdot 2\mathrm{d}, \tag{3}$$

where 2d is the travel distance of the wave, i.e. for one transducer method it is thickness of the sample multiplied by two, τ is the average time of flight and $\mathrm{A_i}$ is the magnitude of i-th echo response.

Complex wave numbers k can be calculated from the phase velocity v and attenuation coefficient α as:

$$\mathrm{k} = \omega/\mathrm{v} + \mathrm{i}\alpha \tag{4}$$

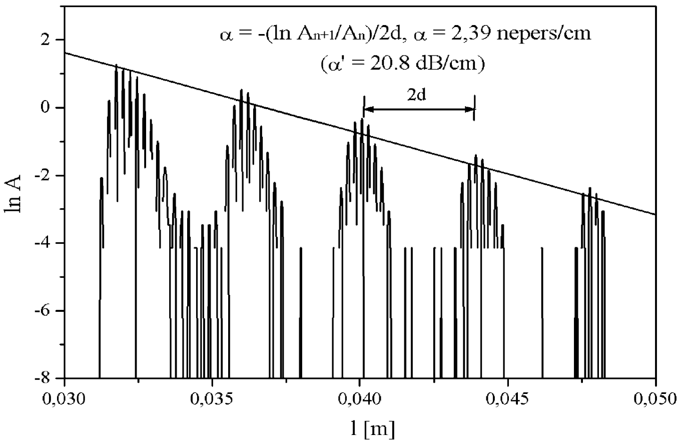

Figure 2. The logarithmic response of PZN: 4.5%PT ⟨001⟩. The slope of the solid line is proportional to α.

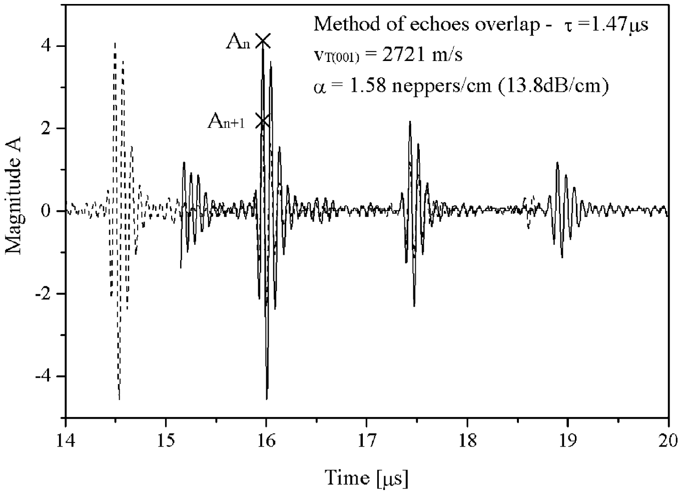

Figure 3. The method of pulse echoes overlap for response of PZN: 4.5%PT ⟨001⟩. The logarithm of ratio of magnitudes A_{i+1}, A_i gives the attenuation α.

Theory

The propagation of a plane wave in solids is governed by Christoffel equation, e.g. [1] and [2]. We can write this equation for piezoelectric solid in this way:

$$\rho v^{2o}u_i = \bar{\Gamma}^{o}_{ij}u_j \tag{5}$$

where $\bar{\Gamma}_{il} = \bar{c}_{ijkl}n_jn_k$ and $\bar{c}_{ijkl} = c^E_{ijkl} + \frac{(e_{pij}n_p)(e_{qkl}n_q)}{\varepsilon^S_{jk}n_jn_k}$.
where c^E_{ijkl}, e_{ijk} and ε^S_{ijk} are the elastic stiffness constants with constant electric field, piezoelectric stress coefficients and dielectric constants of constant strain, respectively. n_i is a component of the unit vector $\vec{n}$ of the wave propagation direction and $^o u_i$ is a component of the direction of particles movement.

Elastic Stiffness Coefficients

Elastic stiffness constants c_{11}, c_{22} and c_{33} (*mm2* symmetry) can be obtained directly by measuring the wave numbers and by launching normally incident longitudinal waves along the principal material axes [3].

$$\text{The pure modes:} \quad c_{ii} = \rho(\omega/k)^2 \quad i = 1, 2, 3 \tag{6}$$

Similarly c_{44} and c_{66}(*4mm* symmetry)

$$c_{44} = \rho(\omega/k)^2 \tag{7}$$

for Z—polarized, Y—propagating, or Y—polarized, Z—propagating waves

$$c_{66} = \rho(\omega/k)^2 \tag{8}$$

for X—polarized, Y—propagating, or Y—polarized, X—propagating waves.

Complex elastic stiffness constant is then expressed from complex wave number (4) as:

$$\bar{c} = \rho \cdot \left(\frac{1}{\frac{1}{\bar{v}} + i \cdot \frac{\bar{\alpha}}{\omega}} \right)^2 \tag{9}$$

The Influence of Polarization

The relations between the velocity and the linear elastic coefficient c_{33}^{E} for a system poled at [001] direction with waves propagating along the [001] direction with contribution piezoelectric effect can be expressed:

$$\rho v_{L,[001]}^2 = c_{33}^E + \frac{e_{33}^2}{\varepsilon_{33}} = c_{33}^E + \frac{4}{\varepsilon_{33}} \left(\left(d_{31} c_{13}^E \right)^2 + d_{31} d_{33} c_{13}^E c_{33}^E + \frac{\left(d_{33}^E c_{33}^E \right)^2}{4} \right) \tag{10}$$

where $c_{\lambda\mu}^E$, $e_{i\lambda}$ and $d_{i\lambda}$ are the elastic stiffness constants with constant electric field, piezoelectric strain coefficients and piezoelectric constants in matrix notation.

For waves propagating along the [110] direction the following relations between the velocities and the linear elastic coefficients c_{11}, c_{12} and c_{44}:

$$\rho v_{L,[110]}^2 = \rho v_{L,[1\bar{1}0]}^2 = (c_{11} + c_{12} + 2c_{44})/2 \tag{11}$$

The phase velocity of the shear wave that propagates along [110] and polarizing in $[\bar{1}10]$ direction is related to elastic stiffness constant:

$$\rho v_{T,[110]}^2 = (c_{11} - c_{12})/2. \tag{12}$$

Experimental Procedure

Samples of the composition 4.5% were prepared. The density of the samples for this composition is 8310 kgm^{-3}. Pulse echo measurements at room temperature were applied to the PZN-PT samples with different crystal orientations. Samples poled during measurements were depoled by annealing at temperature above Curie Weiss temperature T_c and again measured. Modification of ultrasonic pulse echo overlaps method by digitizing of analogue output and consequent numeric processing is used. The commercial $LiNbO_3$ ultrasonic transducers of diameter 0.25″ with delay line for longitudinal and shear sound wave propagation are used. The electric DC bias field was applied by HV amplifier Trek model 610D. Generally thinner samples exhibit much larger values of electric breakdown field, especially thin film layers. For study influence of high field it is necessary used thin samples (0.5–1.0 mm) or thin films. The thickness of samples is limited by frequency of ultrasonic transducer and method of testing.

Various transducers for generation of ultrasound waves were used: a commercial Lithium Niobate transducers (Valpey Fisher, type DP152–0.25″ with polystyrene delay and SD152-FL with fused silica delay) with fundamental frequency 15 MHz for longitudinal and shear wave, small coaxial Lithium Niobate transducers 0.125″ (The Roditi Int. Corp. GMBH) for 10 MHz and a shear wave transducer 7 × 14 mm^2, $LiNbO_3$, with metallic coupling layer to glass delay line working on 22 MHz. The Pulse Modulator & Receiver Model 7700 generated the tone burst pulses and the Plug-in Model 755, 0.5–22 MHz, received R.F. echoes. The ultrasonic system was built on Matec Instruments, Inc. modules. The time domain response was recorded and time of flight between echoes directly measured by digital oscilloscope, type Agilent 54622D. A pulse echo-overlap technique [1] was used for the determination of the absolute velocity values. This technique allows absolute velocities to be obtained with high precision (0.01%).

Electric Field Measurements

The measurement with applied DC bias electric field was realized inside the special sample holder with the bath for breakdown protective liquid, see Fig. 4. We used thin aluminum foil as removable electrodes. Good electric conductivity and mainly ultrasonic coupling is realized by suitable coupling material. A very good material for shear waves coupling at used frequencies is for room temperature a honey.

On Fig. 5 we can observe the process of poling of virgin sample by field applied in [001] direction. The increase of sound velocity of poled compared to unpoled sample is described by second term in Eq. (10) which accounts for the piezoelectric contribution to the elastic constants. Fairly wide range of increases in phase velocity with poling is consistent with ferroelastic domain switching, which was also proposed originally by Cao and Yin [4] and [5]. Clearly, if only 180 domain rearrangements was present during poling, elastic constants would not change in first approximation unless there is unusually large domain wall contribution to the effective elastic constant. However, ferroelastic domain switching is takes place between elastically unequal domains and as consequence the wave velocity changes as a larger volume fraction of crystals is occupied by the domains aligned with the field during poling process. A process of polarization-reversal is also observed once sample

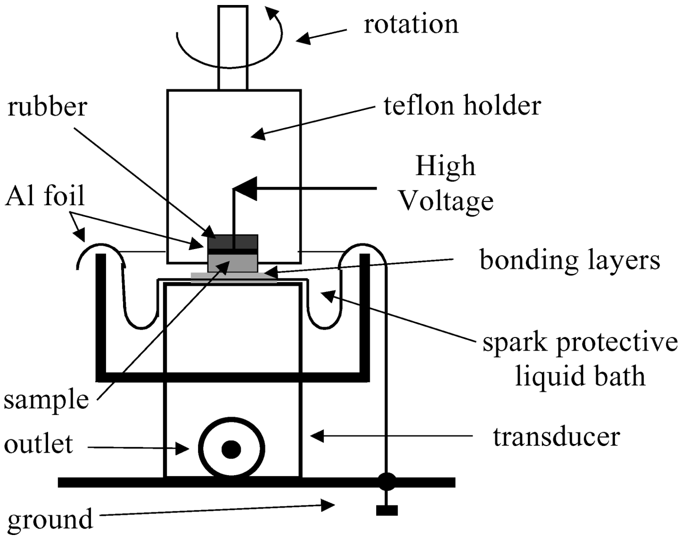

Figure 4. A sample-holder for HV DC bias measurements and rotation dependence of transverse waves.

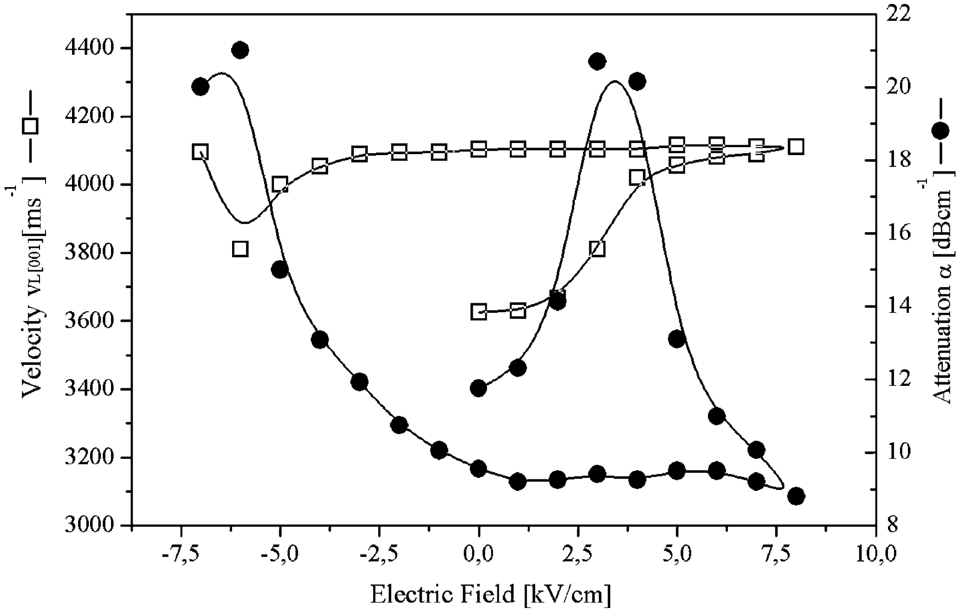

Figure 5. Longitudinal mode velocity and attenuation as functions of Electric field for [001] direction-hysteretic behavior.

is poled and the domains can gradually relax to a lower energy state. Very sensitive physical quantity, which indicates process of depolarization, is delay and attenuation of ultrasound.

On Fig. 6 we can see a narrower process of polarization. We postulate the existence of the field induced macroscopic orthorhombic phase in case of applied field in [110]

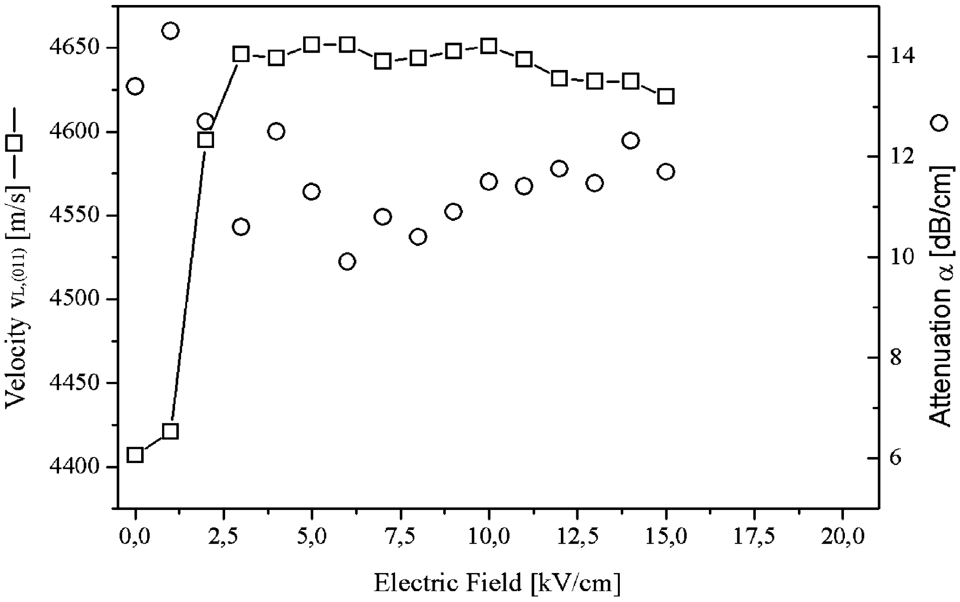

Figure 6. Longitudinal mode velocity and attenuation as functions of electric field for [110] direction.

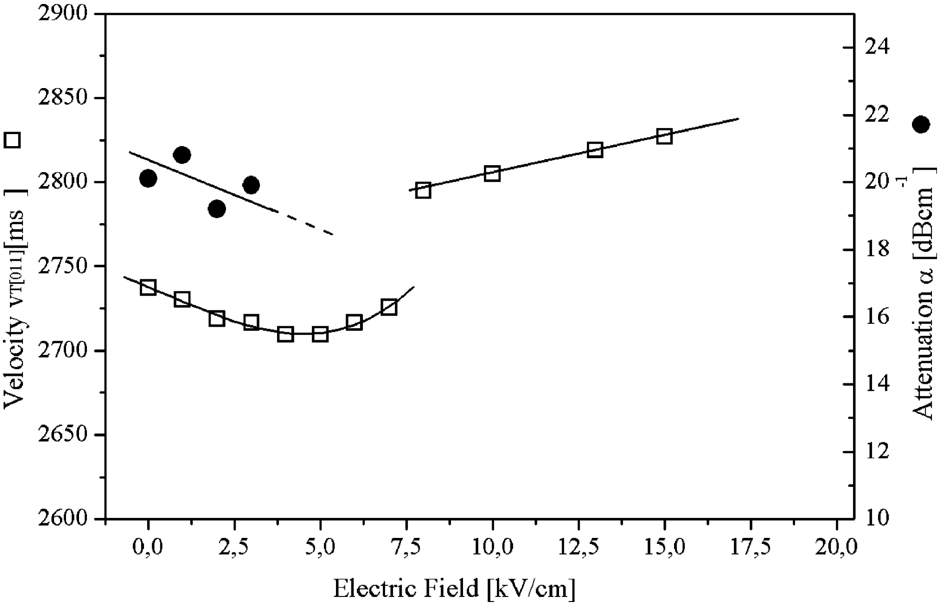

Figure 7. Transverse mode velocity and attenuation as functions of Electric field for [110] direction.

direction. There is a more stable structure for electric field up to 7.5 kV/cm with a reduction in attenuation compared to the unbiased sample. Some instability persists above this field with attendant gradual increase of attenuation and decrease of phase velocity. The instability of domain structure of [110] is also shown in Fig. 7 for transverse mode of wave propagation.

A strong poling process and at very low coercive field is exhibited by [111] sample for electric field applied in [111] direction, see Fig. 8. It is possibly caused by the poling along one of the polar axes of rhombohedral micro-symmetry of the sample at room temperature. It means inducing monodomain state with lower energy along one preferred direction. The increase of attenuation suggests the existence of multi-domain states for lower field up to 5kV/cm. An intermediate phase transition probably to orthorhombic phase changes attenuation above 5 kV/cm. A decrease of the attenuation may correspond to the stabilization of rhombohedral symmetry single domain state above 10kV/cm.

In Table 1 we collected velocity and attenuation measurements in absence of applied electric field for unpoled samples at room temperature. Measurements were performed at a constant electric field $\vec{E}$(clamped conditions). The influence of frequency is studied by comparing results at 15 and 22 MHz for the case of shear wave propagation. All of the results are collected in Table 1. The complex elastic stiffness constants are evaluated using Eq. (9).

Discussion

We can observe the strong influence of relatively small electric fields on phase velocity and attenuation of ultrasound. The almost step change for both parameters is caused by very low coercive field ferroelectric material under study. The change of phase velocity for unpoled and poled state of PZN: 4.5% PT ⟨001⟩ single crystal cut was expressed by Eq. (10) and it is in a good agreement with [4] and [5]. The attenuation of ultrasound propagation seems

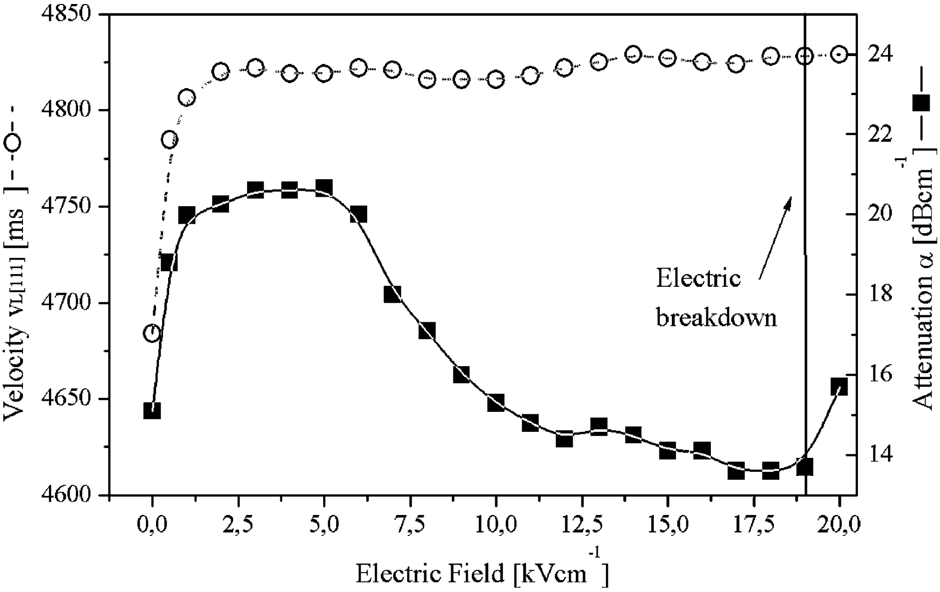

Figure 8. Longitudinal mode velocity and attenuation as functions of electric field for [111] direction.

to be a very sensitive tool for describing of process polarization and domain reorientation in ferroelectric systems.

The domain engineered sample PZN : 4.5% PT cut ⟨001⟩ exhibits at low electric fields step change in speed and attenuation of ultrasound, see Fig. 5. This is caused by domain reorientation of unplowed sample and the consequent stabilization of domain structure.

Table 1

Measured Velocities, Attenuations and Complex Elastic Constants for Logitudinal and Shear Waves at Constant $\vec{E}$. Electricaly Clamped Conditions are Given by Fundamental Frequencies of Used Transducers Which are Operating at 15 and 22 MHz

Sample cut	v_l [m/s]	α [dB/cm]	$\bar{c}^E$ 10^{10} N/m^2	v_s [m/s]	α [dB/cm]	$\bar{c}^E$ 10^{10} N/m^2
001	15 MHz	10.8^{+}	10.7–0.1i	14.7 MHz $2730 \pm 1^{*}$	14.5^{+}	6.19–0.06i
	$3589 \pm 14^{*}$			2721^{**}	13.8^{++}	6.15–0.06i
				22 MHz 2740^{*}	21.2^{+}	6.22–0.06i
110	15 MHz	13.4^{+}	16.1–0.2i	15 MHz $2780 \pm 40^{*}$	14.6^{+}	6.42–0.06i
	$4407 \pm 2^{*}$			22 MHz $2735 \pm 5^{*}$	23^{+}	6.22–0.07i
111	15 MHz	13.9^{+}	18.2–0.3i	***	***	
	$4684 \pm 2^{*}$	14.9^{++}	18.3–0.3i			
	4695^{**}	16^{++}	19.4–0.4i			
	4831^{**} after break					

*linear fit, Eq. (1), **method on Fig. 3, $^{+}$linear fit, Eq. (3) $^{++}$Fig. 3 and Eq. (2), ***not measurable.

In all DC bias electric field measurements we can observe determining influence of poling direction of electric field on process of polarization and induced phase.

The application of high electric fields frequently causes the cracks inside volume of bulk samples. For sample cut ⟨111⟩ was observed electric breakdown at field about 18 kV/cm.

The attenuation of ultrasound exhibits strong frequency dependence for two applied frequencies. For higher frequency the attenuation of single crystals increases. The explanation simply follows from Table 1. The complex impedance of transverse mode measurements for both frequencies was almost the same.

We cannot observe electric field induced phase transition in the sense of the structural phase transition described in [6–8] for very high electric fields exceeding 20 kV/cm. The application of such high electric fields causes the cracks inside thick bulk samples. Probably an enormous stress induced by applied field on large dimensions of samples cannot be compensated. Relatively large samples may include some inclusions and disorders, which can cause local electric breaks downs.

Conclusion

This presentation interests in the ultrasonic methods of measurements and the application of DC bias electric field. The most important for ultrasonic methods is the selection of suitable ultrasonic transducers, bonding material, delay lines if used, an ultrasonic method and numerical processing of measured data.We are using for ultrasonic measurements system MATEC Model 7700 with plug-in working in frequency range up to 22 MHz. Our measurements profit from high mechanical and electrical stability of this system and together with modern computer technique give us ability of high precise measurements.

The study of propagation of the ultrasound in a crystal material enables to complete set of elastic and piezoelectric constants, to study domain reorientation and to estimate presence of structural phase transitions. Electrically clamped conditions are given by high fundamental frequencies of used transducers, which are operating at 15 and 22 MHz.

The ultrasonic methods with applied electric field are powerful tool completing other methods for study of single crystal solid solutions.

Acknowledgments

This work was supported by the Grant Agency of the Czech Republic (Project GACR 202/03/0569) and by the Ministry of Education of the Czech Republic (Project MSM 242200002).

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