



Measurement of thermal depolarization effects in piezoelectric coefficients of soft PZT ceramics via the frequency and direct methods

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ABSTRACT

Depolarization at high temperatures around the Curie point constitutes an important yet difficultly measurable material property of piezoelectric (PZT) ceramics. The common vibrometric technique (d_{33} meters) is not suitable for the measurement of temperature dependences, and therefore we used the frequency method to perform the desired procedures. The indicator selected to show the depolarization state in the piezoelectric ceramics consisted in the piezoelectric charge coefficient, whose value can be effectively measured via the above-mentioned frequency technique. The accuracy of the method was verified via comparing a d_{33} meter constructed by the authors (as described in this paper) and also by means of differently sized cylinders of ceramics NCE51, which are designed for longitudinal length modes. Based on the obtained results, we established a measurement methodology to exactly determine the value of the Curie point that corresponded to the phase transition to a cubic crystallographic structure. The experiment also confirmed the applicability of progressively controlled depolarization of PZT ceramics by high temperature in the range of between 350 and 370 °C, and it defined the temperature limits at which there occur irreversible changes of the piezoelectric properties of PZT ceramics. In the measured NCE51 material, the limit for irreversible changes was equal to 95% of the Curie temperature (368 °C).

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1. Introduction

Piezoelectric ceramics are used as active elements in measurement techniques including, for example, ultrasonic distance sensors, acoustic emission sensors, sensors for crack detection, and high power applications. It is important to know the behavior of the ceramics during exposure to high temperatures near the Curie point, at which the depolarization of PZT elements regularly occurs.

The discussed knowledge of the relationship between parameters of PZT ceramics and temperature appears to be similarly significant in the designing of sensors and active elements by means of simulation and modeling systems, such as the COMSOL and ANSYS software; the said instruments constitute an interactive environment for the modeling and simulation of physical, mechanical, electrical, and other scientific problems. Material property dependences are usually not considered in these systems, and man-

ufacturers do not list them in their data sheets. The heating of PZT ceramics to temperatures close to the Curie point nevertheless causes significant changes of material coefficients and may thus lead to partial or complete depolarization of the ceramics. The entire problem of the temperature dependence of piezoceramics is generally simplified by introducing a limit on the maximum working temperature.

Although the influences of temperature on piezoelectric coefficients and behavior around the Curie point were traditionally a marginal topic rarely discussed in specialized literature, they have recently become a problem of interest to a number of researchers and are currently analyzed in various papers [1–8]. The data related to ceramics NCE51 are not freely available, and only the Curie point value is indicated in this type of material.

Piezoelectricity, and thus also the individual material coefficients, are described in studies [9–13]. Methods for the measurement of material coefficients can be classified into two groups. The first group comprises techniques to determine the complete matrix of coefficients and includes the frequency method [14–17]; the matrix contains piezoelectric, elastic, and dielectric

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coefficients. The second group then consists of methods for the direct measurement of concrete (mostly piezoelectric) coefficients, including the laser interferometer method based on the indirect piezoelectric effect [18–21] or the quasistatic technique applied in d_{33}/d_{31} meters and utilizing the direct piezoelectric effect [22].

The frequency method is currently the most popular approach to determining the complete matrix of coefficients of PZT ceramics. The procedure is described in the European standard EN50324 [23,24], which has been derived from the world standard CEI/IEC 60483: 1976 [25]; both these documents define the measurement techniques and sample dimension requirements in individual types of oscillation. At present, the frequency method involves the application of RLC meters, such as the HIOKI 3532 or the Agilent E4980A. More accurate measurement can be performed with impedance analyzers, for example the Agilent E4294A; this type has been conveniently replaced with the Keysight E4990A and the Wayne Kerr series 6500B. Generally, impedance analyzers allow direct display of the impedance and phase characteristics in real time. This advantage is often utilized in the reading of the resonance (f_r) and antiresonance (f_a) frequencies and enables us to monitor the influence of the clamping of the sample in the tweezers on the impedance characteristics. The drawback of the discussed method consists in the necessity to observe the required minimum proportions of the sample side dimensions for the measured oscillations.

Samples that do not satisfy this requirement are measured by means of direct methods, which usually facilitate the measurement of piezoelectric coefficients and include the laser interferometer technique described in papers [15,18]. The measurement utilizes the inverse piezoelectric effect, in which direct voltage is fed to the sample and a laser interferometer is used to measure the dimension changes. These dimension or displacement changes directly correspond to the magnitude of the exciting voltage. The input voltage, dimension changes, and range of the given interferometer can be used in the calculation of the piezoelectric charge coefficient. The measurement requires either an interferometer assembled from individual components or a full setup, for example the Polytec OFV5000 with a module measuring the displacement within a range of at least 50 nm V^{-1} . The main disadvantage of this approach lies in the necessity to shield the measuring device from external vibrations, which markedly affect the resulting charge coefficient value. Another drawback can be identified in the costly equipment found only in selected laboratories.

The method of direct measurement of the charge on a piezoelectric element during mechanical loading/unloading is based on the direct piezoelectric effect and can be split up into two variants. The first of these is described in paper [15] and uses a special device to calculate the charge coefficient. The piezoelectric element is loaded with a predefined force F in this structure. The charge is measured at piezoelectric unloading either directly by an electrometer (such as the Keithley 6517b) or the output from the piezoelectric element is led via a charge amplifier with a known transfer constant (mV pC^{-1}). The voltage corresponding to the acting force is measured at the output of the amplifier with a multimeter or a signal acquisition module, for example the NI9234.

The other variant exploiting the direct piezoelectric effect is often applied in devices referred to as “ d_{33}/d_{31} meters” [12,13,22]; the manufacturers include KCF Technologies, Sensor Technology Ltd., Piezotest (d₃₃ PiezoMeter Systems), APC International (Wide-Range d₃₃ Tester), HC Materials Corporation, and Concord Electroceramics Industries. Both the permanent excitation of the piezoelectric element by the defined force and the high repeatability are ensured due to the use of a vibration exciter and a reference force sensor.

None of the above-described approaches to the direct measurement of charge coefficients requires intensive shielding of the

Table 1
The dimensions and properties of the samples.

PZT type [-]	Labeling [-]	Diameter (\varnothing) [mm]	Thickness (t) [mm]	d_{33} coefficient $\times 10^{-12} [\text{CN}^{-1}]$
NCE51 no.01	$\varnothing 7.0 \times 15 \text{ mm}$	6.980	15.120	372
NCE51 no.02	$\varnothing 7.0 \times 14.5 \text{ mm}$	6.970	14.550	407
NCE51 no.03	$\varnothing 3.0 \times 5.7 \text{ mm}$	2.968	5.731	411
NCE51 no.04	$\varnothing 3.5 \times 14.5 \text{ mm}$	3.568	14.595	394
NCE51 no.05	$\varnothing 3.5 \times 20 \text{ mm}$	3.487	20.079	371

fixture from external vibrations, and conventional laboratory equipment can be employed to carry out the desired steps.

This paper presents a process of implementing the direct method and discusses the verification procedures related to the measurement conditions, namely the effects of the clamping force and the excitation frequency. The authors also compare the results obtained via the direct and the frequency methods and investigate whether the frequency method provides sufficient accuracy for measuring material coefficients of PZT ceramics at higher temperatures, or under circumstances that disallow any reliable use of the direct method.

2. Experiments

2.1. Materials

The cylindrical samples of soft piezoelectric ceramics with silver electrodes (or discs) were obtained from Noliac Ceramics. This commercial type of PZT ceramics with the general chemical formula $\text{Pb}(\text{Zr}_{0.52},\text{Ti}_{0.48})\text{O}_3$ was assigned the trade name NCE 51. The Curie temperature stated by the manufacturer equals to $360 \pm 18^\circ\text{C}$, and the value of the piezoelectric d_{33} coefficient at 25°C for the longitudinal length mode is equal to 443 pCN^{-1} with tolerances of $\pm 5\%$ [26]. The geometrical dimensions and labelling of individual samples are shown in Table 1. The samples were selected in such a manner that the proportions of height differ with respect to the cylinder base diameter. Different dimensions of the measured samples and various batches of the manufactured piezoceramics have a significant effect on the deviation in the d_{33} coefficient. At present, the manufacturing process is often fully automated, but even despite this, the actual production is still affected by biases in material coefficients of the ceramics. Thus, it cannot be guaranteed that, in the given type of the product, the resulting material coefficient values will always correspond to the reference values, which are usually obtained for a single concrete batch and dimension of the piezoelectric ceramics. The reference values of the piezoelectric charge coefficients (the d_{33} coefficient) were determined via the frequency method described in one of our previous publications [15].

2.2. Determination of the piezoelectric charge coefficients

2.2.1. Direct vibrometric measurement of the reference piezoelectric charge coefficients of the samples

Firstly, the relationship between the piezoelectric charge coefficient and the magnitude of the force F_3 acting vertically on the sample at the constant exciting frequency of 110 Hz was measured. The basic range of the set forces F_3 (from 0.1 N to 7 N) does not affect the charge coefficient significantly; any disruption of the integrity of the ceramics or, possibly, their complete destruction requires a pressure of tens or hundreds of MPa [27–29].

The configuration of the setup for direct measurement of the charge coefficient d_{33} by means of a laboratory d_{33} meter is shown in Fig. 1. The experimental setup was composed of a vibration exciter Brüel & Kjær (B&K) type 4809, with a reference force sensor B&K 8200 fixed to the vibrating centre of the exciter.

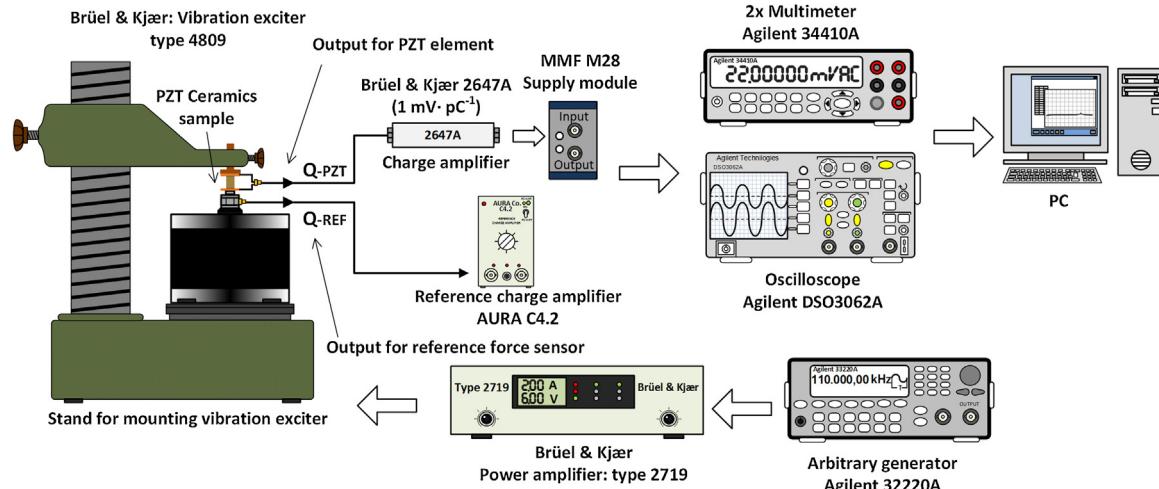


Fig. 1. Measurement of the d_{33} piezoelectric charge coefficients via the direct charge measuring method.

The force sensor output was led via a reference charge amplifier AURA C4.2 with preset tenfold amplification to a multimeter Agilent 34410A. The measured piezoelectric element was placed between the reference force sensor and the upper arm of the exciter. The charge generated at the electrodes of the measured sample was conducted via a charge amplifier B&K 2647A to the multimeter Agilent 34410A. The signals from both the sensor and the measured piezoelectric element were simultaneously displayed by an Agilent DSO3062A oscilloscope, and the observed waveforms enabled us to check the clamping of the element between the contact electrodes. The measured data were communicated via USB interface to an application in LabVIEW. The vibration exciter was controlled by an arbitrary generator Agilent 32220A operating in conjunction with a power amplifier B&K 2719.

The piezoelectric charge coefficient d_{33} for the cylinder is calculated using the formula

$$d_{33} = \frac{U_{PZT}}{F_3 \times K_q} = \frac{U_{PZT}}{\frac{U_{SENSOR}}{K_{SENSOR} \times K_{q-sensor}}} \times K_q, \quad (1)$$

where d_{33} (CN^{-1}) is the piezoelectric charge coefficient, F_3 (N) is the force applied to an element in the direction 3, U_{PZT} (V) is the output voltage of the piezoelectric element measured on the multimeter Agilent 34410A after being amplified via the charge amplifier BK2647A having the sensitivity of $k_q = 1 \text{ mV pC}^{-1}$, and U_{SENSOR} (V) is the output voltage of the force transducer BK 8200 exhibiting the sensitivity of $k_{SENSOR} = 3.93 \text{ pC N}^{-1}$; this voltage is measured via the multimeter Agilent 34410A after being amplified with the charge amplifier AURA C4.2, whose sensitivity is $k_{q-SENSOR} = 10 \text{ mV pC}^{-1}$.

2.3. Temperature measurement of material coefficients in the examined piezoelectric ceramics

Fig. 2 shows the block diagram for the measurement of temperature dependences and presents the setup to ensure partial depolarization in the piezoelectric ceramics, which were polarized in Lukosiol M50 silicone oil at 1.5 kV mm^{-1} and 140°C . The heating and depolarization based on high temperatures are performed with a GEMINI 700LRI dry block calibrator by AOIP; the device features the adjustable range of between 30°C and 700°C and the absolute stability of $\pm 0.05^\circ\text{C}$. The calibrator is connected to a PC, on which an application in LabVIEW is run, via the RS422/RS232 interface. The application facilitates the sensing and setting of the chamber temperature; the temperature is independently monitored by a digital thermometer Greisinger GMH 3230 equipped with a thermocou-

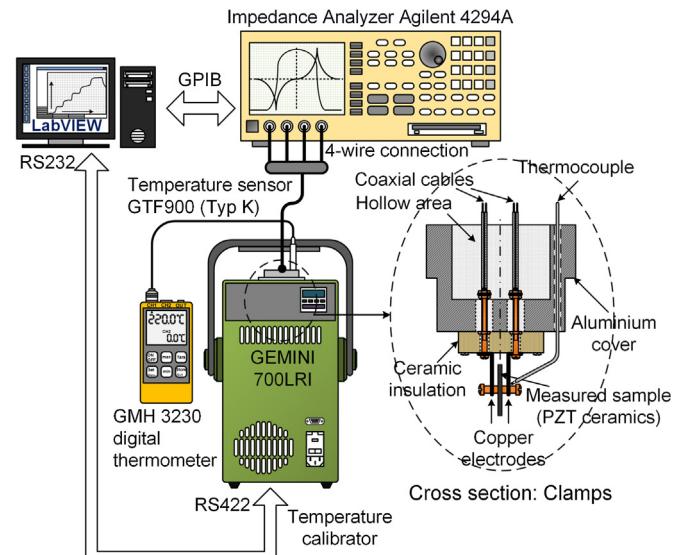


Fig. 2. The connection diagram for the measurement of temperature dependences and thermal depolarization in PZT ceramics.

ple GTF900 (type K), and this thermocouple is in direct contact with the electrode holding the sample. The experiments showed that the maximum difference between the surface temperature of the sample and the temperature measured on the electrode corresponded to 3°C . Within the following stage of the set-up procedure, the measured sample of PZT ceramics is connected via four conductors to the input of the impedance analyzer Agilent 4294A, which is linked with the PC through GPIB. The impedance analyzer enables us to measure the basic parameters of the ceramics, namely the resonance and antiresonance frequencies, the free capacity at 1 kHz , and the dissipation factor $\tan \delta$. The input data measurement is then performed by the application in LabVIEW. The obtained input parameters and geometrical dimensions of the measured sample of piezoelectric ceramics can be utilized to calculate the entire matrix of material coefficients, which consists of piezoelectric, elastic, and dielectric coefficients. The actual clamping of the sample is ensured by special tweezers designed in such a manner that they can be placed directly into the dry block calibrator; a cross section through the tweezers is shown in Fig. 2 [30]. The design of the tweezers facilitates their use in another calibrator, namely a HYPERION Basic by AOIP. The HYPERION device is connected to a

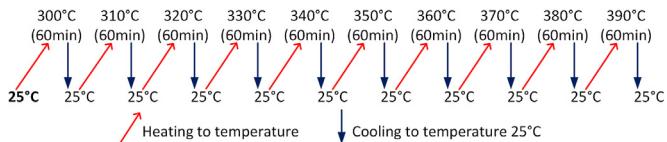


Fig. 3. The step-by-step temperature measurement procedure in an NCE51 piezoelement cylinder ($\varnothing 7 \times 15$ mm).

PC via the RS422/RS232 interface and allows temperature setting between -20°C and 140°C with the stability of $\pm 0.03^{\circ}\text{C}$. This calibrator is instrumental for cooling the PZT elements down to the reference value of 25°C .

To measure the temperature dependences, we utilized the frequency method, whose advantage consists in the possibility of measuring the parameters of PZT ceramics directly in the calibrator. On this basis, we were subsequently able to measure the influence of the temperature on the resonance and antiresonance frequencies of the measured sample at the instantaneous temperature.

2.3.1. Measurement of the Curie temperature

Before the actual temperature depolarization, it was necessary to establish the Curie temperature of the applied piezoelectric ceramics. The manufacturer of the PZT ceramics specifies the Curie temperature value equal to 360°C ; however, we need to note that the manufacturer-specified values are often lower than the real Curie temperature, and such lower temperatures are presented deliberately for safety reasons. The design of the devices then respects the lower Curie temperature values. If the operating temperature of the ceramics reaches these values, the material remains unharmed and unaffected by lasting internal changes. The temperature dependence within the range from 260°C to 410°C was measured for the free capacity C^T at 1 kHz, loss factor $\tan \delta$ at 1 kHz, and relative permittivity ε_{3r} , which is calculated from the geometrical dimensions and free capacity C^T of the measured sample.

2.3.2. Influence of the heating time on the stabilization of the coefficients

In the dry block calibrator, the measured sample of PZT ceramics was surrounded by air. A digital thermometer GMH 3230 was used to establish the instantaneous temperature in the measured sample. The time required to heat the complete volume of each sample was defined experimentally as the period after which the material coefficients do not occur any additional changes. In the experimental case, the applied sample showed the size of $\varnothing 7 \times 15$ mm. The time required for complete heating of the ceramics was established according to the thermal diagram in Fig. 3.

The measured sample of piezoelectric ceramics was inserted into the dry block calibrator GEMINI, in which the required temperature had been preset. After inserting the PZT element into the device, we used the impedance analyzer Agilent E4294A to measure the input parameters for the calculation of the material coefficients; the measurement was performed at the interval of 0 to 60 min with the pace of $2\frac{1}{2}$ minutes. The presented pace had been selected with respect to the time required for the measurement with the impedance analyzer. Then, after 60 min, the sample was removed from the GEMINI and inserted into the HYPERION dry block calibrator, in which the temperature had been preset to 25°C . When the ceramics cooled down to 25°C , the electrical parameters of the ceramics were measured again. The temperature range of the measurement was selected according to the Curie point established in the given sample of PZT ceramics (NCE 51, $\varnothing 7 \times 15$ mm); the resulting range then oscillated between 300°C and 390°C , which remains within the Curie temperature (368°C) of the given sample. Based on the described measurement, we set up a diagram defining the relationship between the behavior of the piezoelectric

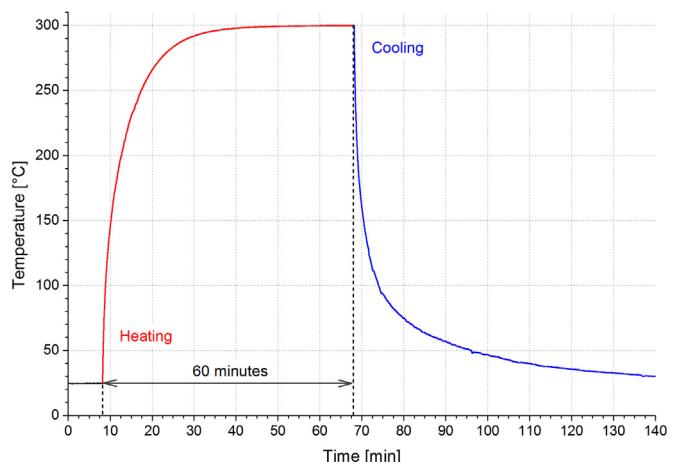


Fig. 4. An example of the behavior of heating and cooling at the selected temperature of 300°C .

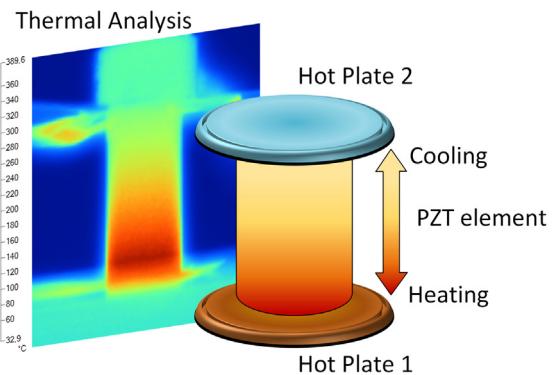


Fig. 5. A thermogram of the cylindrical piezoelectric ceramics ($\varnothing 7 \times 15$ mm) during partial depolarization via a temperature gradient.

ceramics and the heating time. The obtained graphical representation thus indicates the heating time necessary for the parameters of the measured sample to stabilize at the given temperature.

An example of the real behavior of the temperature measured with the thermocouple on the surface of the sample at the transition between the reference temperature of 25°C and the required temperature of 300°C is shown in Fig. 4. We did not observe any impact of the temperature growth speed upon the resulting mechanical properties of the sample. After the actual temperature cycling, the samples were polarized, and the obtained frequency characteristics did not exhibit any major changes (unlike the characteristics measured before depolarization).

2.4. Methods of partial thermal depolarization

These thermal effects include also the partial depolarization caused by heating the PZT ceramics up to temperatures approaching the Curie point. An example of both a temperature gradient applied to the piezoelectric ceramics and their partial depolarization is shown in Fig. 5. This effect may occur if the ceramics, either as an individual element or as a complete sensor, are placed on a surface heated to a high temperature. In such a situation, the depolarization is not complete but merely partial. In practical applications, partial depolarization often constitutes a spurious effect, but in some cases it can be a desired instrument to facilitate controlled modification of certain material coefficients. The central problem of partial depolarization consists in finding a suitable procedure to measure the instantaneous status of the process. This can be ensured only with good knowledge of not only the behavior of

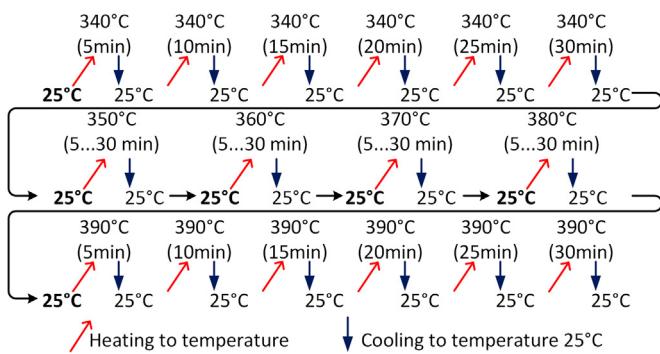


Fig. 6. The measuring process for the cylindrical piezoelement sample of $\varnothing 7 \times 15$ mm: heating the ceramics and cooling them down to 25°C .

Chapter II: Results and Discussion

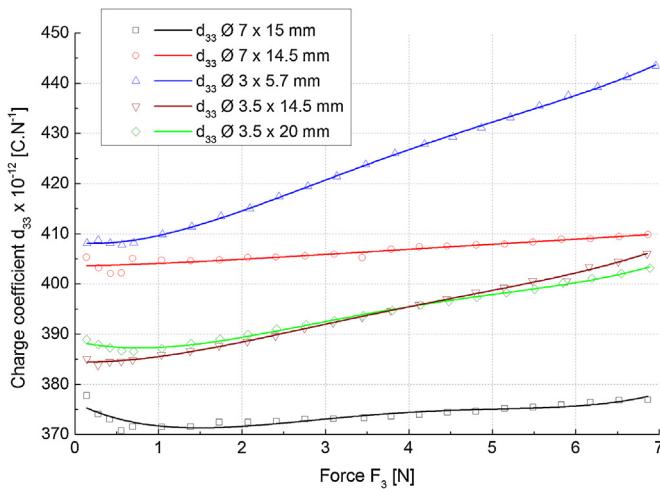


Fig. 7. The dependence between the piezoelectric charge coefficient d_{33} and the applied force F_3 on the measured piezoelectric element (d_{33} for samples with $\varnothing 7 \times 15$ mm (\square), $\varnothing 7 \times 14.5$ mm (\circ), $\varnothing 3 \times 5.7$ mm (\triangle), $\varnothing 3.5 \times 14.5$ mm (∇), and $\varnothing 3.5 \times 20$ mm (\diamond)).

PZT ceramics at high temperatures near the Curie point but also the methods for exact determination of the coefficient according to which the degree of depolarization is measured. The given purpose can be achieved via the above-defined direct method utilizing a d_{33} meter or by means of the frequency method.

Partial depolarization of the PZT ceramics via high temperature is performed using the setup demonstrated in Fig. 6. The final measurements of the heating time then point to the fact that the ceramics are heated gradually, and it is therefore possible to apply the principle indicated in Fig. 6, where partial depolarization based on high temperature is shown. If the PZT ceramics are kept in the calibrator for a certain time, the material will be partially heated; the temperature in the vicinity of the centre is then denoted as T_1 , while the corresponding conditions at the edge are expressed as T_2 . If we have $T_2 > T_1$, and assuming that T_2 equals the Curie temperature or a higher value, complete depolarization of the entire PZT ceramics will not occur; however, partial depolarization will be observed at the edge of the piezoelectric element. If there holds $T_2 = T_1$, complete depolarization of the entire sample of PZT ceramics will appear, as expected. Thus, we may conclude that partial depolarization can be regulated to a certain extent, yet only if the related preconditions are satisfied. In this context, above all, the Curie temperature of the given piezoelectric sample must be established in advance, and the impact of the heating time and temperature on the PZT element must be known.

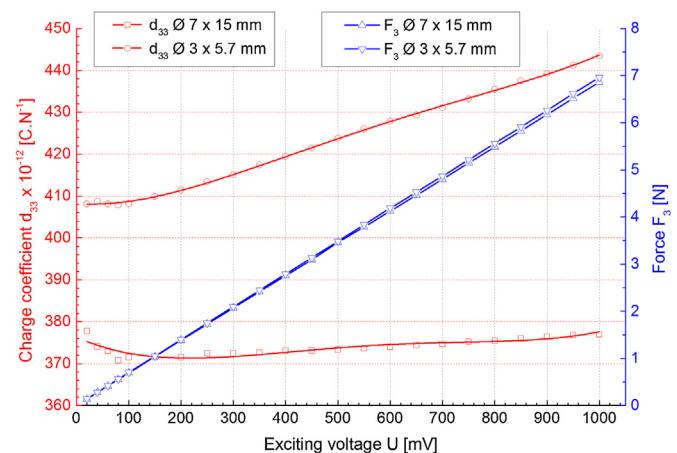


Fig. 8. A comparison of the piezoelectric charge coefficients d_{33} for cylinders with the parameters of $\varnothing 7 \times 15$ mm and $\varnothing 3 \times 5.7$ mm; the diagram indicates the behavior of the force F_3 acting on the samples at the reference value of the exciting voltage. For $\varnothing 7 \times 15$ mm we have the charge coefficient d_{33} (\square) and force F_3 (\triangle), while for $\varnothing 3 \times 5.7$ mm there applies the charge coefficient d_{33} (\circ) and force F_3 (∇).

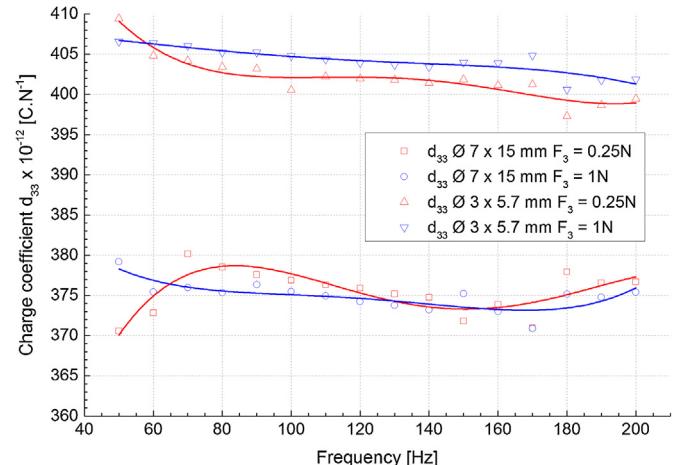


Fig. 9. A comparison of the piezoelectric charge coefficients d_{33} for cylinders with the parameters $\varnothing 7 \times 15$ mm and $\varnothing 3 \times 5.7$ mm depending on the change of the exciting frequency for the forces of 0.25 N and 1 N. Parameters in the graph: 0.25 N (\square), 1 N (\circ) corresponded to the sample $\varnothing 7 \times 15$ mm and 0.25 N (\triangle), 1 N (∇) corresponded to the sample $\varnothing 3 \times 5.7$ mm.

Partial depolarization via temperature cannot ensure steady growth of the piezoelectric coefficients; it can only guarantee their decrease to a value corresponding to the preset temperature. The discussed approach is therefore not applicable in increasing the values of PZT ceramics coefficients but can be used for other purposes, such as the creation of a gradient waveform of the piezoelectric charge coefficient d_{33} along the entire length of the PZT element. If one side of the element exhibits the original value of the piezoelectric charge coefficient d_{33-01} , then this value is gradually decreased along of the length element to d_{33-02} , and subsequently there holds $d_{33-01} \gg d_{33-02}$.

Partial depolarization by means of a temperature wave was performed according to the diagram in Fig. 6. The piezoelectric element was inserted in the GEMINI dry block calibrator to be maintained at the preset temperature for the defined time, removed, inserted in the HYPERION calibrator, and cooled down to 25°C . This procedure was then repeated at intervals of between 5 and 30 min, with the temperatures ranging from 340°C to 390°C . Both the intervals and the temperature range were selected on the basis of the results obtained from the measurement of the PZT element heating time, Figs. 11–13. After each temperature cycle, namely heating

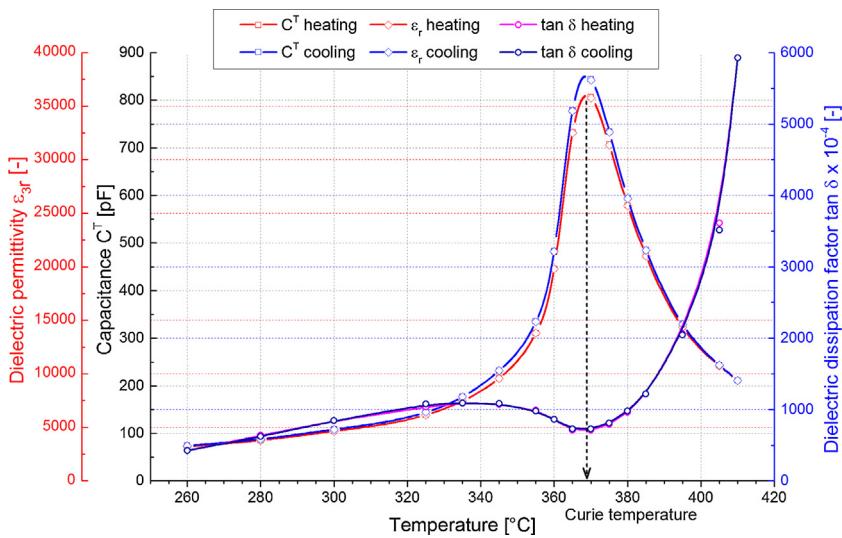


Fig. 10. The temperature dependence of the relative dielectric permittivity ε_{3r} (\diamond), free capacity C^T (\square), and dielectric dissipation factor $\tan \delta$ (\circ) in the sample of $\varnothing 7 \times 15$ mm.

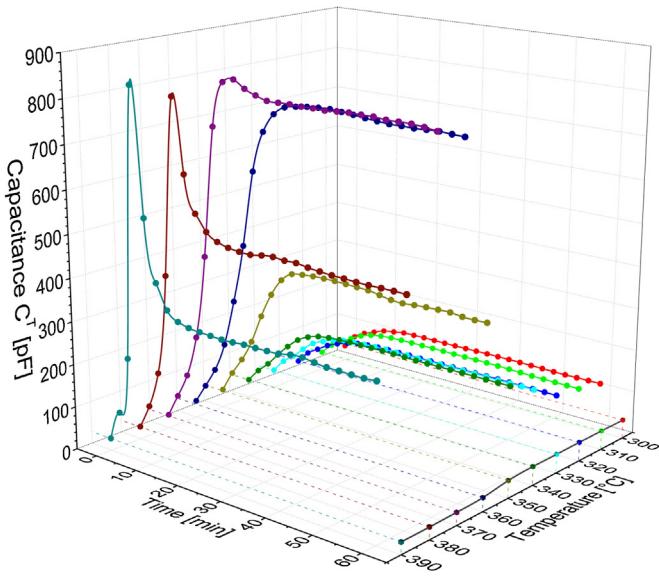


Fig. 11. The effect of the heating time in the sample of $\varnothing 7 \times 15$ mm upon the free capacity C^T measured at 1 kHz for the temperature range of between 300°C and 390°C .

the ceramics and cooling them down to the ambient temperature, the sample was measured via the direct vibrometric method, using a laboratory-made d_{33} meter; the results were later compared with the values acquired by means of the frequency measurement method.

2.4.1. Direct measurement of partial depolarization via the vibrometric method

The piezoelectric charge coefficient values acquired through partial depolarization were measured via the direct method, using a laboratory-made d_{33} meter for two values of the force F_3 at the constant exciting frequency of 110 Hz. First, we selected the force of 0.25 N, which is generally used in d_{33} meters available on the market. The other force value was set to 1 N. The setting of 1 N, namely a force four times higher than the initial 0.25 N, was carried out to facilitate comparison of the two resulting charge coefficient values and to eliminate possible errors in the reading of small values of the force F_3 .

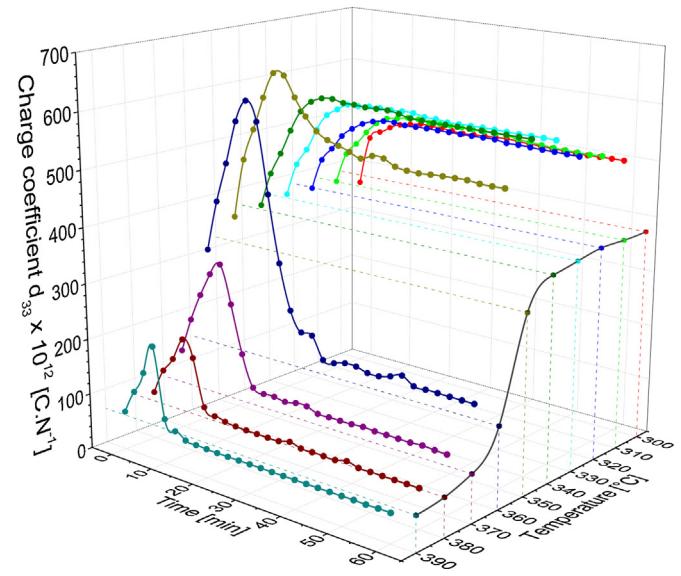


Fig. 12. The effect of the heating time in the sample of $\varnothing 7 \times 15$ mm upon the charge coefficient d_{33} for the temperature range of between 300°C and 390°C .

2.4.2. Direct measurement of partial depolarization via the frequency method

The piezoelectric charge coefficients were measured and subsequently calculated from the resonance frequency, free capacity C^T (1 kHz), density, and geometric dimension according to the Formula (2) below, which had been derived from the European standard EN50324-2 [24].

$$d_{33} = k_{33} \left(\varepsilon_{33}^T \times s_{33}^E \right)^{\frac{1}{2}} = \left(\varepsilon_{33}^T \times s_{33}^D \times \frac{k_{33}^2}{1 - k_{33}^2} \right)^{\frac{1}{2}} \\ = \left(C^T \times \frac{t}{\frac{\pi \times d^2}{4}} \times \frac{1}{4 \times \rho \times f_a^2 \times t^2} \times \frac{\frac{\pi}{2} \times \frac{f_r}{f_a} \times \tan \left(\frac{\pi}{2} \times \frac{f_a - f_r}{f_a} \right)}{1 - \frac{\pi}{2} \times \frac{f_r}{f_a} \times \tan \left(\frac{\pi}{2} \times \frac{f_a - f_r}{f_a} \right)} \right)^{\frac{1}{2}} \quad (2)$$

where d_{33} (CN^{-1}) is the piezoelectric charge coefficient, k_{33} (–) is the longitudinal coupling factor, ε_{33}^T (Fm^{-1}) is the permittivity, s_{33}^E and s_{33}^D ($\text{m}^2 \text{N}^{-1}$) are the elastic compliance coefficients, C^T (F) is the free capacitance measured at 1 kHz, d (m) is the diameter, t (m) is the thickness, and f_r and f_a (Hz) are the resonant and antiresonance frequencies.

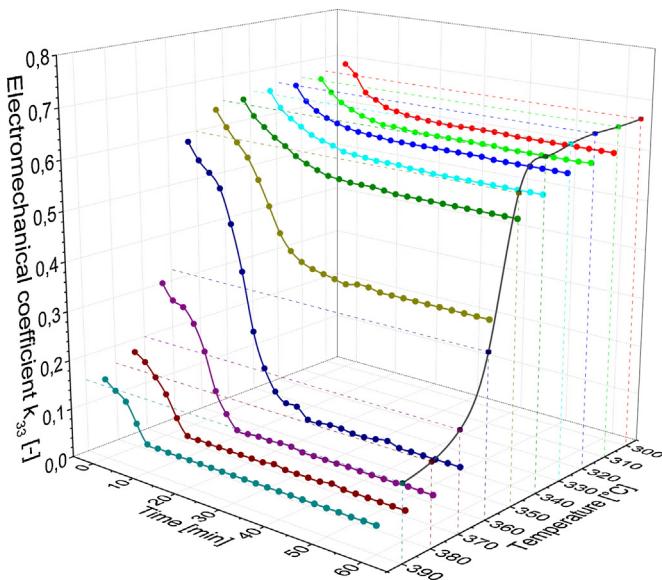


Fig. 13. The effect of the heating time in the sample of $\varnothing 7 \times 15$ mm upon the electromechanical coupling coefficient k_{33} for the temperature range of between 300°C and 390°C .

The impedance analyzer Agilent 4294A and the measuring clamps in Fig. 2 were used for the input data measurement. We applied the same temperature conditions as in the previously discussed vibrometric method.

3. Results and discussion

3.1. Direct vibrometric measurement of the reference piezoelectric charge coefficients of the samples

In most currently produced d_{33} meters, the parameters for the testing of the measured piezoelectric samples are set such that the generated force equals 0.25 N and the exciting frequency corresponds to 110 Hz. The force acting on the sample was adjusted to minimize its influence on the coefficient of charge of the measured material. The dependences of the piezoelectric charge coefficient d_{33} on the force applied to the samples are shown in Fig. 7. The magnitude of the force F_3 was set via changing the amplitude of the exciting signal from the generator. The preset values then oscillated between 0.14 N and 6.8 N. Given these limit values, we found out that the acting force does not markedly affect the resulting charge coefficient within the range of 0.2 N to 1 N. Above 1 N, however, the influence of the force on the crystal structure of the examined ceramics begins to show, and the charge coefficient gradually increases.

If the force acting on the sample is small (approximately 0.25 N), the result may be affected by error in the measurement of the given force and by the reading of the output voltage of the charge amplifier. Both these errors can be eliminated through using a force sensor with ample resolution for small force ranges or by applying a charge amplifier providing a higher amplification rate. The output voltage can be suitably measured by means of a multimeter or a signal acquisition module with sufficient resolution, such as the Agilent 34410A or the National Instruments NI 9234, respectively. In the described case, the oscilloscope (according to the diagram in Fig. 1) is utilized only to monitor the measured signal from the force sensor and the measured piezoelectric element; it is not applicable for the actual measurement due to insufficient accuracy of the voltage measuring procedure.

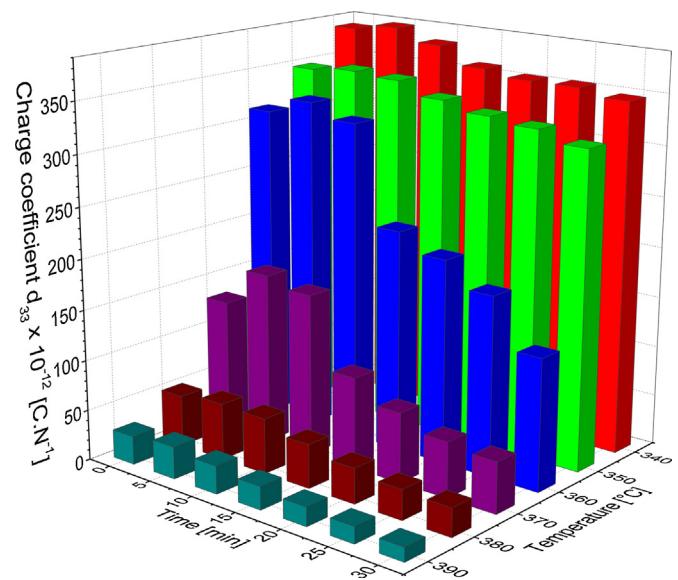


Fig. 14. The resulting effect of thermal depolarization on the piezoelectric charge coefficient d_{33} for the PZT element of $\varnothing 7 \times 15$ mm, measured with a d_{33} meter at $F_3 = 0.25$ N.

For the above-mentioned cylinders, Fig. 8 shows in detail the waveform characterizing the relationship between the charge coefficient d_{33} and the acting force F_3 via the reference value of voltage from the generator. This voltage was utilized as the reference in all measurements of the effect of the force F_3 on the charge coefficient. The dimensions of both samples were chosen with respect to the marked difference between these dimensions and the individual dependences of the charge coefficient on the increasing force F_3 .

In the examined samples, $\varnothing 7 \times 15$ mm and $\varnothing 3 \times 5.7$ mm, we then measured the relationship between the charge coefficients and the exciting frequency of the vibration exciter. The cylinders were measured at the force F_3 equalling 0.25 N and 1 N, for exciting frequencies of between 50 Hz and 200 Hz. The force F_3 was selected based on the previous measurement, where significant error occurred in measuring the force F_3 at values below 0.25 N; conversely, at values above 1 N we could already observe the influence of the force F_3 on the charge coefficient. The frequency range was derived from the reference value of the frequency 110 Hz used in the previous measurement. The resulting behavior of the relationship between the charge coefficient d_{33} and the exciting frequency is presented in Fig. 9. The largest measurement error occurs at low frequencies (50 Hz to 70 Hz) and within the range of between 150 Hz and 200 Hz, where it attains the maximum at around 2%. Thus, there does not occur any significant measurement error within the entire selected range. The use of an exciting frequency at approximately 110 Hz does not markedly affect the resulting value of the charge coefficient d_{33} .

3.2. Measurement of temperature dependences around the Curie temperature

The PZT ceramics were measured during the heating phase and then also while being cooled down to the initial temperature of 260°C . The entire thermal diagram is presented in Fig. 10. At each attainment of the required temperature, the sample was kept at the given temperature to stabilize for the period of 20 min, and subsequently its parameters were measured using the impedance analyzer. The Curie temperature is generally defined as the temperature value at the maximum capacity C^T , and, according to the

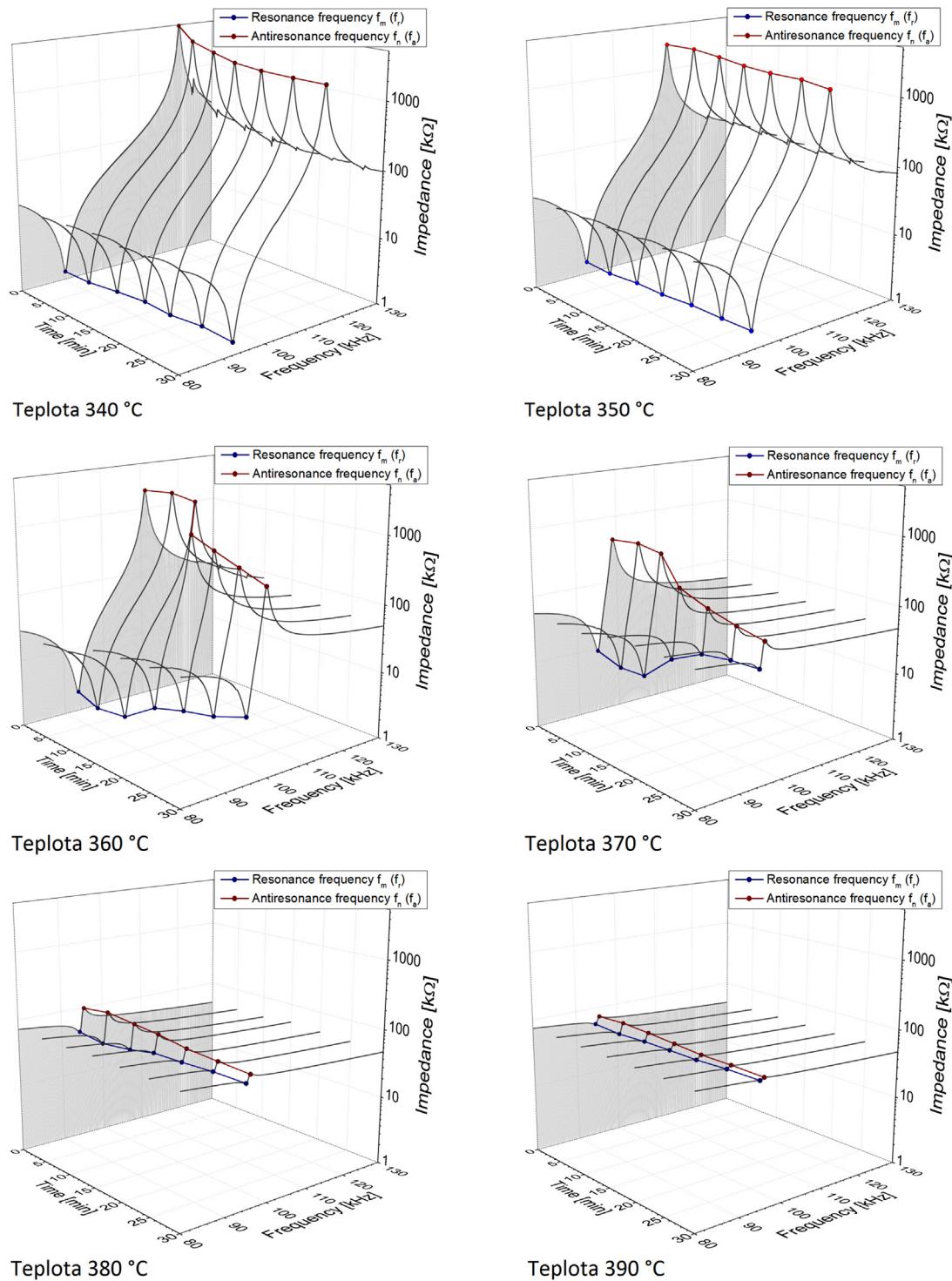


Fig. 15. The waveforms of the resonance and antiresonance frequencies measured with the impedance analyzer Agilent 4294A during partial depolarization via temperature in the PZT element of $\varnothing 7 \times 15$ mm.

European standard EN50324-1 [23], it should be read only after the sample has been cooled down. The difference between the Curie temperatures obtained during the heating or cooling phases remains merely minimal if the sample is kept at each preset temperature for the time required to stabilize the parameters of the ceramics. In this case, the temperature at the maximum value of the capacity C^T , or ε_{3r} , equals 368°C , which corresponds to the temperature range specified by the manufacturer of the ceramics.

3.3. Influence of the heating time on the stabilization of the coefficients

Fig. 11 shows the effect of the heating time together with the time required to stabilize the value of the free capacity C^T at the preset temperature. The data are further complemented with the waveform of the resulting value of the free capacity C^T measured invariably after cooling the ceramics down to the temperature of

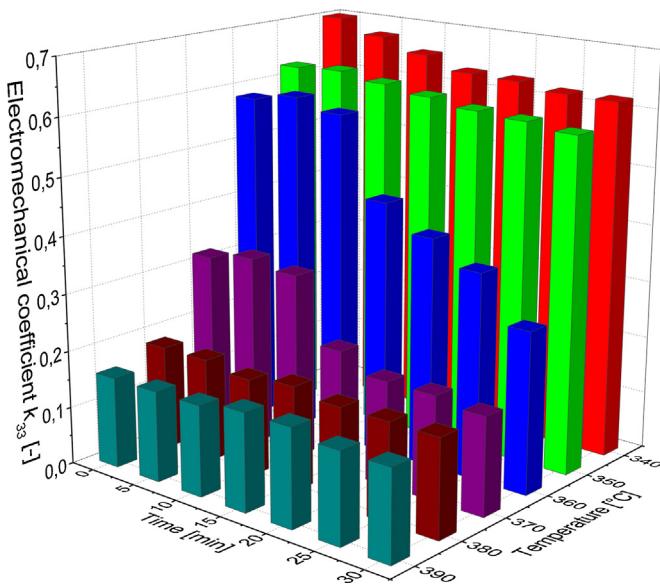


Fig. 16. The resulting effect of temperature depolarization upon the electromechanical coefficient k_{33} for the PZT element of $\varnothing 7 \times 15$ mm, measured with the frequency method.

25 °C; this waveform is represented as a curve which, after the end of the 60 min measurement, passes along the axis of the temperature and connects the resulting values obtained from the individual measurements of C^T after the stabilization at 25 °C. The actual measurement exhibits a marked influence of the Curie point vicinity on the values of the free capacity C^T , which attains its maximum during the transition of the Curie point. As is shown in the same figure, the resulting capacity value returns to its original value after the cooling phase. Small deviations in the values of C^T can be caused by the evaporation of humidity from the ceramics samples in the course of heating or by the oxidation of lead inside the material.

When approaching the phase transition from a monoclinic or a tetragonal structure to a cubic structure (also known as the Curie point), we observe an increase in the maximum values of the piezoelectric charge coefficient. This coefficient was calculated from the resonance frequency and free capacity C^T , using the above Formula (2) shown in Section 2.4.2.

The decrease in the piezoelectric coefficient down to the complete loss of the piezoelectric material properties, namely depolarization, occurs after heating above the Curie point. In contrast, the electromechanical coefficient (electromechanical coupling factor) decreases with increasing temperature in its entirety due to the relative approximation of the resonance and antiresonance frequencies.

The temperature effect is apparent also in the resulting value of the piezoelectric charge coefficient d_{33} presented in Fig. 12 below. The charge coefficient already exhibits the influence of partial depolarization of the PZT element; if the temperature approaches the Curie point, there occur irreversible changes of the charge coefficient even after cooling the element back to 25 °C. During heating, the charge coefficient attains its maximum precisely at the Curie point before starting to decrease significantly with the temperature growth. The diagrams indicate the possibility of lowering the coefficient constantly until the required value is reached.

The direct influence of heating on the resonance frequencies of the given PZT element can be observed in the electromechanical coefficient k_{33} , which is calculated directly from the resonance and antiresonance frequencies. As in the charge coefficient d_{33} , a marked decrease occurs also in the electromechanical coefficient k_{33} in the vicinity of the Curie point (Fig. 13). A temperature

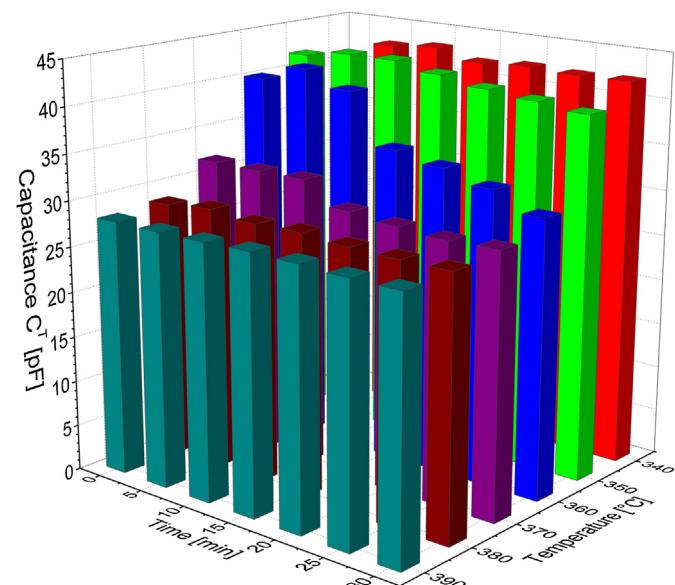


Fig. 17. The resulting effect of temperature depolarization upon the capacity C^T measured at 1 kHz for the PZT element of $\varnothing 7 \times 15$ mm, obtained with the frequency method.

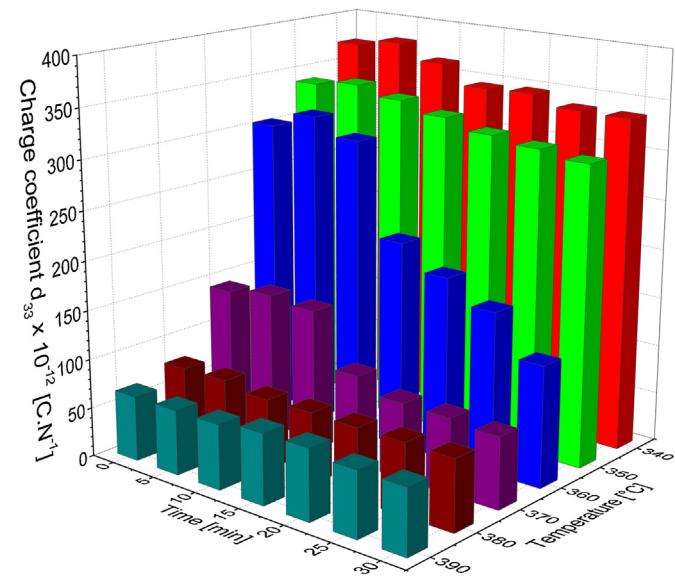


Fig. 18. The resulting effect of temperature depolarization on the piezoelectric charge coefficient d_{33} for the PZT element of $\varnothing 7 \times 15$ mm, measured with the frequency method.

increase is then accompanied by a decrease in not only the difference between the resonance and antiresonance frequencies but also the resulting amplitude. This effect is directly proportional to the growth of temperature, and if the PZT element is heated to the Curie temperature, we can observe irreversible changes of the resonance and antiresonance frequencies until the resonance and the piezoelectric properties of the element cease to exist.

Based on the results obtained from the measurement of the time necessary to stabilize the PZT element at the currently set temperature, it is possible to determine the time required for the stabilization of the measured piezoelectric element ($\varnothing 7 \times 15$ mm). The time needed to stabilize the piezoelectric element at the temperature oscillates between 25 and 30 min; after this period, no major changes occur in the behavior of the material coefficients of the ceramics. The waveforms shown in Figs. 11 and 13 can be used

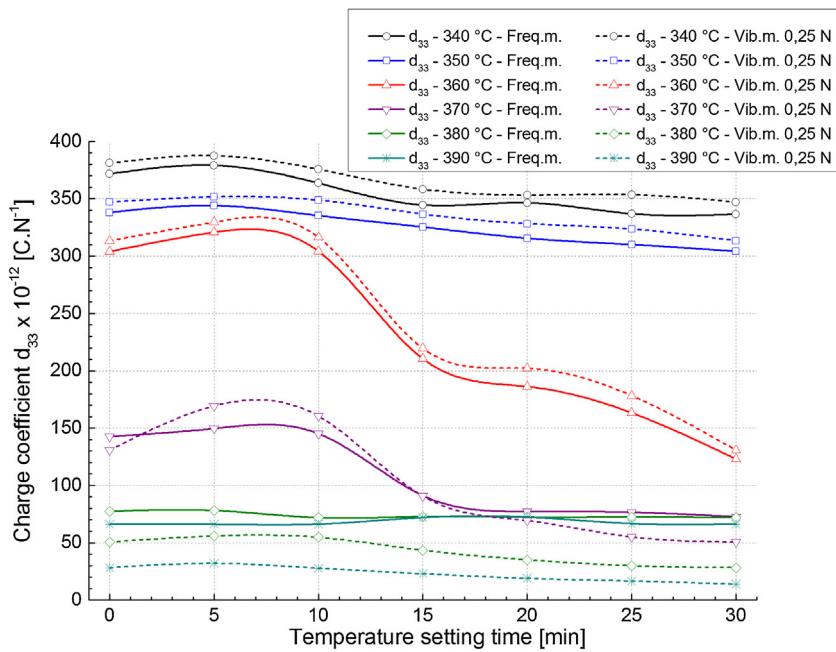


Fig. 19. A comparison of the direct vibrometric method (dashed line) utilizing a laboratory-made d_{33} meter and the frequency method (solid line) in measuring the piezoelectric charge coefficient d_{33} during partial temperature depolarization for 340 °C (○), 350 °C (□), 360 °C (△), 370 °C (▽), 380 °C (◊), and 390 °C (*).

in estimating the behavior of the ceramics at temperatures close to the Curie point. The measured ceramics were markedly depolarized only at 380 °C, which means that they can be utilized to a certain extent even in the region above the Curie point; however, before any such use, it is necessary to consider the time during which the ceramics will be exposed to the given temperature and to respect the volatility of the material coefficients together with their eventual decrease.

3.4. Comparison of the vibrometric and frequency methods for the measurement of partial depolarization

3.4.1. The vibrometric method

The resulting values of the piezoelectric charge coefficient d_{33} for the force of 0.25 N are shown in Fig. 14. The effect of the change of the acting force remains beyond the capabilities of the method. The most prominent decrease of the charge coefficient occurs at 360 °C, a temperature corresponding to the Curie point of the measured PZT ceramics. The resulting value, and thus also the degree of depolarization, can be regulated by the time during which the sample is kept at the preset temperature inside the calibrator. If a marked change of the charge coefficient (and therefore a high degree of depolarization) is required, the sample must be present in the calibrator for a sufficient time; alternatively, a higher temperature can be set to heat the sample only briefly. If the temperature is set significantly high above the Curie point, namely to a value between 380 °C and 390 °C in the given case, there do not occur any marked changes of the charge coefficient d_{33} , and the PZT ceramics are almost depolarized in this region. The effect of the acting force F_3 is minimal within the entire measurement range, and major differences cannot be observed even at very low values of the charge coefficient d_{33} .

3.4.2. The frequency method

Using this approach, the charge coefficient is not measured directly, and it is therefore possible to observe also the influence of temperature on the input parameters measured with an impedance analyzer. Fig. 15 shows the impedance characteristics for the longitudinal type of oscillations in the PZT element of Ø 7 × 15 mm

within the temperature range from 340 °C to 390 °C. The dependences are measured (always after cooling the sample down to the reference temperature of 25 °C inside the HYPERION calibrator) according to the diagram of gradual depolarization presented in Fig. 14.

After calculating the electromechanical coupling coefficient k_{33} from individual waveforms of the impedance characteristics, we can observe the total influence of depolarization on the PZT element. The mutual approximation of the resonance and antiresonance frequencies is caused by a change of the piezoelectric charge coefficient d_{33} . Direct variation of the resonance frequencies can be expressed by the electromechanical factor k_{33} , which is calculated from the difference of the resonance and antiresonance frequencies. The depolarization procedure of the electromechanical coefficient is presented in Fig. 16. The effect of the change of the capacity C^T depending on the degree of depolarization (Fig. 17) is minimal compared to the marked variation in the electromechanical coefficient k_{33} . All displayed values are measured again only after the PZT element has cooled down to the reference temperature of 25 °C.

The resulting value of the piezoelectric coefficient d_{33} obtained via the frequency method is shown in Fig. 18; here, the marked decrease of the charge coefficient value in the vicinity of the Curie point corresponds to the mutual approximation of the resonance and antiresonance frequencies. Above 370 °C there did not occur almost any changes in the capacity C^T or in resonance, and the sample was completely depolarized during further temperature growth.

3.4.3. A comparison between the vibrometric and frequency methods

A direct comparison of the two methods used to acquire the piezoelectric charge coefficient d_{33} exhibits strong agreement up to 370 °C, namely slightly above the value of the Curie point. Above the Curie temperature, the value of the piezoelectric charge coefficient d_{33} decreases such that, in both methods, it is possible to identify the shortcomings that may affect the final value of the coefficient d_{33} . In direct measurement with the applied d_{33} meter, the signal generated by the PZT element is very weak, and therefore also the

real signal-to-noise ratio remains small. In the frequency method, errors manifest themselves during the reading of the resonance and antiresonance frequencies from the impedance characteristics of the PZT element. The resulting comparison of the frequency method and the direct technique utilizing a d_{33} meter at 0.25 N and 110 Hz within the entire depolarization range is shown in Fig. 19; generally, in this context, it is possible to point out that the frequency method is not suitable for use at low values of the piezoelectric charge and electromechanical coefficients.

4. Conclusion

The aim of the performed experiments was to provide a detailed description of the behavior of the soft $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics manufactured under the trade name NCE51. During the research, we focused on the behavior phase related to the actual transition exceeding of the Curie point. Material coefficients of the piezoelectric ceramics can be markedly influenced by the action of high temperatures. The growing temperature may exceed the Curie point, potentially causing partial or complete depolarization of the PZT element. The momentary status of depolarization can be monitored directly via the piezoelectric charge coefficient, which visibly indicates the progress of depolarization in the volume of the piezoelectric element. To determine the charge coefficient, we utilized basic methods for the measurement of material coefficients of piezoelectric ceramics. The most widely used techniques, which were also applied in the measurement and are closely described in this paper, include the frequency and direct methods based on the direct piezoelectric effect. The former approach was selected as the primary technique for determining the piezoelectric charge coefficient, mainly because it is characterized by high accuracy and (compared to the latter method) simpler applicability in the measurement of temperature dependences of piezoelectric ceramics. The direct technique, then, is beneficial in cases where the measurement with the frequency method could be affected by erroneous setting of the charge coefficient. The method was chosen based on the possibility of directly measuring the piezoelectric charge coefficient; thus, we do not need to consider the error caused by calculating the charge coefficient from the input measured parameters. The disadvantage of the discussed approach consists in its problematic use for measurement at high temperatures. Using the values of the piezoelectric charge coefficient acquired from both techniques, we were able to define the influence of temperature on the depolarization of the soft PZT ceramics; the results then indicated that the ceramics could be depolarized only partially, in the immediate vicinity of the Curie point. Partial depolarization via temperature in the volume, possibly depolarization based on a temperature wave, facilitates the formation of the charge coefficient gradient, whose magnitude may oscillate between the initial value of the charge coefficient of the originally polarized sample and a value approaching zero.

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References

- [1] R.G. Sabat, B.K. Mukherjee, W. Ren, G. Yang, Temperature dependence of the complete material coefficients matrix of soft and hard doped piezoelectric lead zirconate titanate ceramics, *J. Appl. Phys. Dielectr. and Ferroelectr.* 101 (6) (2007), <http://dx.doi.org/10.1063/1.2560441>, 064111:1–7.
- [2] F. Li, Z. Xu, X. Wei, X. Yao, Determination of temperature dependence of piezoelectric coefficients matrix of lead zirconate titanate ceramics by quasi-static and resonance method, *J. Phys. D: Appl. Phys.* 42 (9) (2009) 7, <http://dx.doi.org/10.1088/0022-3727/42/9/095417>.
- [3] C. Miclea, C. Tanasoiu, L. Amarande, M. Cioangher, L. Trupina, C.T. Miclea, C. David, Temperature Dependence of the Main Piezoelectric Parameters of a Nb-Li Doped PZT Ceramic, International Semiconductor Conference 2006, Bucharest, National Inst. Mater. Phys., 2, 279–282. ISBN 1-4244-0109-7, **10.1109/SMICND.2006.283997**.
- [4] C. Miclea, C. Tanasoiu, C.F. Miclea, L. Amarande, M. Cioangher, L. Trupina, A. Luga, I. Spanulescu, C.T. Miclea, C. David, M. Susu, Behaviour of the main properties of hard and soft type piezoceramics with temperature from 2 to 600 K, *Int. Semicond. Conf. (CAS)* 2 (2010) 301–304, <http://dx.doi.org/10.1109/SMICND.2010.5650718>, ISBN: 978-1-4244-5783-0.
- [5] J. Chen, H. Shi, G. Liu, J. Cheng, S. Dong, Temperature dependence of dielectric, piezoelectric and elastic properties of $\text{BiScO}_3\text{-PbTiO}_3$ high temperature ceramics with morphotropic phase boundary (MPB) composition, *J. Alloys Compd.* 537 (2012) 280–285, <http://dx.doi.org/10.1016/j.jallcom.2012.05.041>.
- [6] J. Ilg, S.J. Rupitsch, R. Lerch, Temperature measurements by means of the electrical impedance of piezoceramics, 2012, IEEE Int. Instrum. Meas. Technol. Conf. (I2MTC) (2012) 1851–1855, <http://dx.doi.org/10.1109/I2MTC.2012.6229130>.
- [7] J. Erhart, L. Rusin, L. Seifert, Resonant frequency temperature coefficients for the piezoelectric resonators working in various vibration modes, *J. Electroceram.* 19 (4) (2007) 401–403, <http://dx.doi.org/10.1007/s10832-007-9062-1>, Special Issue on Piezoelectric for End Users II.
- [8] L. Burianová, A. Kopal, J. Nosek, Characterization of advanced piezoelectric materials in the wide temperature range, *Mater. Sci. Eng. B* 99 (1–3) (2003) 187–191, [http://dx.doi.org/10.1016/S0921-5107\(02\)00490-7](http://dx.doi.org/10.1016/S0921-5107(02)00490-7).
- [9] B. Jaffe, W.R. Cook Jr., H. Jaffe, *Piezoelectric Ceramics*, Academic Press, London and New York, 1971, pp. 315, ISBN 0-12-379550-8.
- [10] A. Arnau, *Piezoelectric Transducers and Applications*, Second edition, Springer-Verlag, Germany, 2008, pp. 548, <http://dx.doi.org/10.1007/978-3-540-77508-9>, ISBN 978-3-540-77507-2.
- [11] J. Tichy, J. Erhart, E. Kittinger, J. Privratska, *Fundamentals of Piezoelectric Sensors: Mechanical, Dielectric, and Thermodynamical Properties of Piezoelectric Materials*, Springer, 2010, <http://dx.doi.org/10.1007/978-3-540-68427-5>, p. 207, 978-3-540-43966-0.
- [12] APC International, *Piezoelectric Theory and Applications Piezoelectric Ceramics: Principles and Applications*, American Piezo Ceramics Inc., 2002, 112 p., ISBN 0-9718744-0-9.
- [13] J.W. Waanders, *Piezoelectric Ceramics: Properties and Applications*, 1st edition, Philips Components Eindhoven, The Netherlands, 2016, pp. 4–91, ISBN 9398-651-80011.
- [14] S. Sherrit, T.J. Masys, H.D. Widerick, B.K. Mukherjee, Determination of the reduced matrix of the piezoelectric, dielectric, and elastic material constants for a piezoelectric material with C_{oo} symmetry, *IEEE Ultrason. Ferroelectr. Freq. Control* 58 (9) (2011) 1714–1720, <http://dx.doi.org/10.1109/TUFFC.2011.2008>.
- [15] J. Fialka, P. Benes, Comparison of methods for the measurement of piezoelectric coefficients, *IEEE Trans. Instrum. Meas.* 62 (5) (2013) 1047–1057, <http://dx.doi.org/10.1109/TIM.2012.2234576>.
- [16] International Standard: IEEE Standards on Piezoelectricity, ANSI/IEEE Std 176–1987, The Institute of Electrical and Electronics Engineers, Inc 1987 66 p., <http://dx.doi.org/10.1109/IEEESTD.1988.79638>.
- [17] C. Wenwu, Z. Shining, J. Bei, Analysis of shear modes in a piezoelectric vibrator, *J. Appl. Phys.* 83 (8) (1998) 4415–4420, <http://dx.doi.org/10.1063/1.367233>.
- [18] L. Burianová, M. Šulc, M. Prokopová, Determination of the piezoelectric coefficients d_{ij} of PZT ceramics and composites by laser interferometry, *J. Eur. Ceram. Soc.* 21 (10–11) (2001) 1387–1390, [http://dx.doi.org/10.1016/S0955-2219\(01\)00024-3](http://dx.doi.org/10.1016/S0955-2219(01)00024-3).
- [19] A. Saad, Y. Jiang, Y. Liu, Z. Wang, The measurement of the diameter change of a piezoelectric transducer cylinder with the white-light interferometry, *Opt. Laser. Eng.* 56 (2014) 169–172, <http://dx.doi.org/10.1016/j.optlaseng.2014.01.005>.
- [20] S.J. Rupitsch, R. Lerch, Inverse Method to estimate material parameters for piezoceramic disc actuators, *Appl. Phys. A Mater. Sci. Process.* 97 (2009) 735–740, <http://dx.doi.org/10.1007/s00339-009-5438-1>.
- [21] S.J. Rupitsch, A. Sutor, J. Ilg, R. Lerch, Identification procedure for real and imaginary material parameters of piezoceramic materials, *IEEE International Ultrasonics Symposium Proceedings* (2010) 1214–1217, <http://dx.doi.org/10.1109/ULTSYM.2010.5935504>.
- [22] J. Erhart, L. Burianová, What is really measured on a d_{33} -meter? *J. Eur. Ceram. Soc.* 21 (2001) 1413–1415, [http://dx.doi.org/10.1016/S0955-2219\(01\)00030-9](http://dx.doi.org/10.1016/S0955-2219(01)00030-9), Elsevier Science Ltd.
- [23] European Standard, EN 50324-1, 2002, Piezoelectric properties of ceramic materials and components, Part 1: Terms and definitions, CENELEC European Committee for Electrotechnical Standardization, 2002.
- [24] European standard, EN 50324-2, 2002, Piezoelectric properties of ceramic materials and components, Part 2: Methods of measurement—Low power, CENELEC European Committee for Electrotechnical Standardization, 2002.

[1] R.G. Sabat, B.K. Mukherjee, W. Ren, G. Yang, Temperature dependence of the complete material coefficients matrix of soft and hard doped piezoelectric

- [25] International Standard, CEI/IEC 60483, 1976, Guide to dynamic measurements of piezoelectric ceramics with high electromechanical coupling, IEE Geneva, Switzerland, 1997, 40 p., ICS 31.140.
- [26] NOLIAC, Piezo ceramics specification—Piezo Materials Ver.1404 [online], <http://www.noliac.com>.
- [27] J. Zhao, Q.M. Zhang, Effect of mechanical stress on the electromechanical performance of PZT and PMN-pT ceramics, ISAF '96 Proceedings of the 10th IEEE International Symposium on Applications Of Ferroelectrics 2 (1996) 971–974, <http://dx.doi.org/10.1109/ISAF.1996.598190>, ISBN 0-7803-3355-1.
- [28] G. Yang, W. Ren, S.-F. Liu, A.J. Masy, B.K. Mukherjee, Effects of uniaxial stress and DC bias field on the piezoelectric, dielectric, and elastic properties of piezoelectric ceramics, IEEE Ultrason. Symp. 2 (2000) 1005–1008, <http://dx.doi.org/10.1109/ULTSYM.2000.921494>, ISBN 0-7803-6365-5.
- [29] S. Sherrit, D.B. Van Nice, J.T. Graham, B.K. Mukherjee, H.D. Wiederick, Domain wall motion in piezoelectric materials under high stress, Proc. Appl. Ferroelectr. 2 (1992) 167–170, <http://dx.doi.org/10.1109/ISAF.1992.300653>, ISBN 0-7803-0465-9.
- [30] J. Fialka, P. Benes, S. Pikula, S. Klusacek, Measurement of temperature dependence in material coefficients of PZT ceramics for acoustic emission sensors, IEEE ultrasonics, ferroelectrics, frequency control society and European frequency and time, IUS Proc. (2013) 1109–1112, <http://dx.doi.org/10.1109/ULTSYM.2013.0284>, ISBN: 978-1-4673-5686-2.