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Dispersion characteristics of complex electromechanical parameters of porous piezoceramics

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In this paper, the results of experimental study of dispersion characteristics of complex electromechanical parameters of ferroelectrically "hard" porous piezoceramics based on PZT composition were presented. Experimental samples of porous piezoceramics were fabricated using a modified method of burning-out a pore former. The complex constants of porous piezoceramics with relative porosity 16% and their frequency dependences were measured using the piezoelectric resonance analysis method. As a result of experimental studies, regions of elastic, piezoelectric and electromechanical dispersion, characterized by anomalies in the frequency dependences of the imaginary and real parts of the complex constants of porous piezoelectric ceramics were found. It was revealed also that the microstructural features of porous piezoceramics determine the character of frequency dependences of complex electromechanical parameters of porous piezoelectric ceramics. In conclusion, the microstructural and physical mechanisms of electromechanical losses and dispersion in porous piezoceramics were discussed.

Keywords: Porous piezoceramics; microstructure; dispersion; losses; complex electromechanical constants.

1. Introduction

In recent years, the requirements for the functional characteristics of piezoelectric materials have increased significantly.[1]

New monocrystalline, piezoceramic and piezocomposite materials are widely used in piezoelectric and ultrasonic transducers with high sensitivity, efficiency and resolution.[2,3] Some of these advanced materials have high dielectric, piezoelectric and mechanical losses, accounting for the out-of-phase material response to the input signal and demonstrate nonlinear behavior.

Electromechanical losses and dispersion are one of the main physical parameters that determine the possibility of using piezoelectric materials in modern ultrasonic, piezoelectric and acoustoelectronic devices.[4]

Porous piezoceramics based on different piezoceramic compositions are one of the relatively new promising piezoelectric materials that are important for many technical applications, such as ultrasonic transducers and sensors for medical diagnostics and therapy, nondestructive testing, underwater acoustics, etc.[5,6]

Intensive research and technological work, as well as the development of new manufacturing methods made it possible to organize the mass production of porous piezoelectric ceramics with controlled and reproducible porosity and electromechanical properties.[7,8]

Porous ceramics are heterogeneous media with unique microstructures that provide original, effective dielectric, elastic and electromechanical properties.[9] Elastic losses and dispersion in porous piezoceramics and piezocomposites have been studied in a number of works.[10,11] Based on the analysis of general relationship between ultrasonic attenuation and dispersion, it was found that Rayleigh scattering of elastic waves on pores causes elastic dispersion in a porous piezoceramics.

However, despite numerous studies, many aspects of the frequency dependences of the complex electromechanical parameters, as well the microstructural and physical mechanisms of electromechanical losses and dispersion in porous piezoceramics are still unclear.

In this work, we studied dispersion characteristics of complex elastic, piezoelectric and electromechanical parameters of ferroelectrically "hard" porous piezoceramics based on the PZT system.

2. Experimental Techniques

Ferroelectrically "hard" PZT-type piezoelectric ceramics of the composition $PbTi_{0.41}Zr_{0.49}Nb_{0.057}Zn_{0.0235}W_{0.006}Mn_{0.011}O_3$ + 0.1% GeO_2 with relative porosity 16% and average pore size of 30 μm were chosen as the object of the study. Experimental samples of porous piezoceramics were obtained using a

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modified method of pore formers burning-out.[7] Porosity and pore size distribution were determined using the stereology and hydrostatic weighing methods.

The porous ceramics samples with fired silver electrodes were poled in air by applying to the electrodes a dc electric field (1.5 kV/mm) at heating above Curie temperature (340 °C) and then cooling to room temperature.

Microstructural studies were fulfilled on grinded and chipped surfaces of the porous piezoceramic samples using scanning electron microscope (SEM, Karl Zeiss and TM-100, Hitachi).

The complex elastic, dielectric and piezoelectric parameters of the piezoceramics elements were measured using Agilent 4294A impedance analyzer and the piezoelectric resonance analysis software (PRAP).[12] The frequency dependences of complex dielectric, piezoelectric and electromechanical parameters of the experimental samples of porous piezoceramics were studied by successive analyzing the impedance spectra for the fundamental and higher-order resonances of thickness vibrational mode using the PRAP software.

The method we have developed[13–15] allows measurements and analysis of the results in the high frequency ranges, for which the fabrication of porous piezoceramic elements operating on the fundamental mode of thickness oscillations is impossible because of a small thickness and fragility.

3. Results and Discussion

3.1. *Microstructure study*

Micrographs illustrating the main features of the porous piezoceramics microstructure are shown in Figs. 1 and 2. According to the images, the porous piezoceramics are characterized by random distribution of irregular shape pores with the average size of 30 μm.

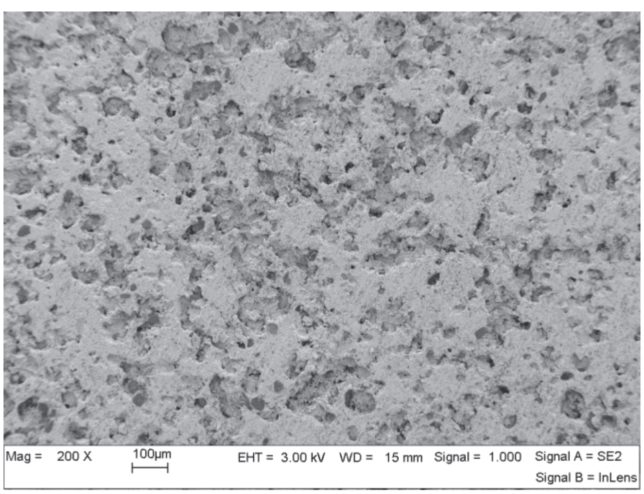

Fig. 1. SEM image of grinded surface of the porous piezoceramics with the relative porosity 16%.

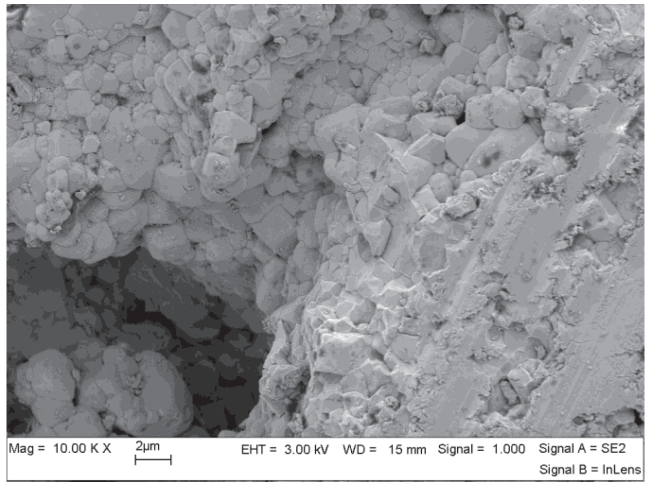

Fig. 2. Microstructure of the porous piezoceramics with the relative porosity of 16%.

It can be seen from the micrographs that the ceramic microstructure is characterized by dense packing of grains with average size 2–3 μm that does not differ from the grain size observed for dense piezoceramics of the same composition.

These micrographs demonstrate the presence in porous piezoceramics of a rigid three-dimensional (3D) piezoceramics frame with continuous quasi-rod structure that determines the main features of its electromechanical properties.

3.2. *Electromechanical properties study*

Figures 3 and 4 show measured impedance spectra and PRAP approximations for the thickness and radial vibrational mode of the porous piezoceramic disk Ø7 × 0.82 mm with a relative porosity of 16%.

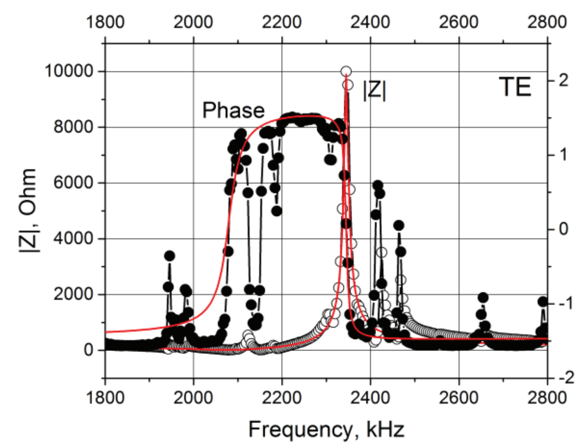

Fig. 3. The impedance spectra and PRAP approximations for the thickness vibrational mode of the porous piezoceramic disk Ø7 × 0.82 mm with a relative porosity of 16%.

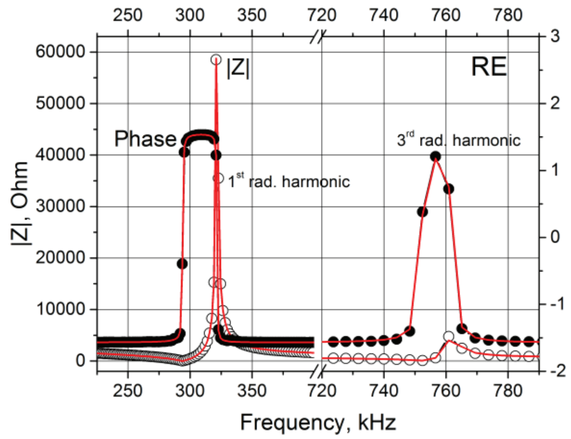

Fig. 4. The impedance spectra and PRAP approximations for the radial vibrational mode of the porous piezoceramic disk Ø7 × 0.82 mm with a relative porosity of 16%.

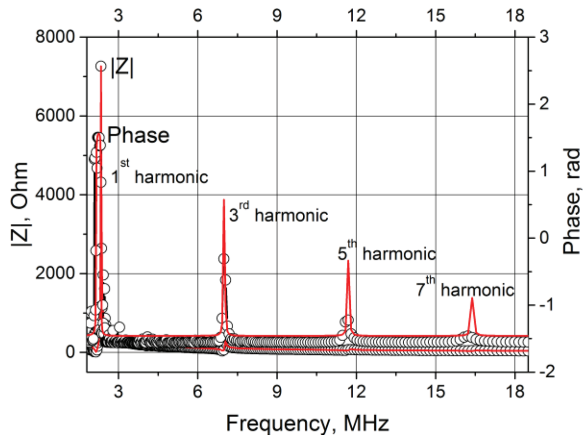

Fig. 5. The impedance spectra and PRAP approximations for the seventh harmonics of the thickness vibrational mode of the porous piezoceramic disk Ø7 × 0.82 mm with a relative porosity of 16%.

The complex dielectric, piezoelectric and elastic parameters of the porous piezoceramics derived from the measured impedance spectra for radial and thickness vibrational modes of the piezoceramics disks are listed in Table 1.

Table 1. The complex electromechanical parameters of the porous piezoceramics of the composition $PbTi_{0.41}Zr_{0.49}Nb_{0.057}Zn_{0.0235}W_{0.006}Mn_{0.011}O_3$ + 0.1% GeO_2 with relative porosity 16%.

Parameter	Real	Imaginary
Radial extensional (RE) mode		
f_s (Hz)	$2.94 \cdot 10^5$	315
S_{11}^E (m²/N)	$1.92 \cdot 10^{-11}$	$7.57 \cdot 10^{-14}$
S_{12}^E (m²/N)	$-7.81 \cdot 10^{-12}$	$5.35 \cdot 10^{-14}$
$-d_{31}$ (C/N)	$1.00 \cdot 10^{-10}$	$4.44 \cdot 10^{-13}$
ε_{33}^T (F/m)	$8.22 \cdot 10^{-9}$	$2.38 \cdot 10^{-11}$
k_p	0.44	0.00131
σ^p	0.408	0.00118
e_{31} (C/m²)	8.83	0.0219
S_{66}^E (m²/N)	$5.39 \cdot 10^{-11}$	$2.58 \cdot 10^{-13}$
C_{66}^E (N/m²)	$1.85 \cdot 10^{10}$	$8.884 \cdot 10^7$
Thickness extensional (TE) mode		
f_s (Hz)	$2.08 \cdot 10^6$	$2.14 \cdot 10^4$
k_t	0.5	0.0145
C_{33}^D (N/m²)	$9.91 \cdot 10^{10}$	$3.63 \cdot 10^8$
C_{33}^E (N/m²)	$7.43 \cdot 10^{10}$	$1.71 \cdot 10^9$
e_{33} (C/m²)	14.1	1.21
h_{33} (V/m)	$1.75 \cdot 10^9$	$5.44 \cdot 10^7$
ε_{33}^S (F/m)	$8.05 \cdot 10^{-9}$	$9.41 \cdot 10^{-10}$

Figure 5 shows the measured impedance spectra and PRAP approximations for the fundamental and high-order resonances of thickness vibrational mode of the porous piezoceramic disk Ø7 × 0.82 mm with a relative porosity of 16%. It is obvious from Fig. 5 that each high-order resonance peaks are clearly delineated, which makes it possible to perform PRAP analysis to obtain the frequency dependences of the complex parameters of porous piezoelectric ceramics.

Figures 6–8 show the frequency dependences of complex elastic, piezoelectric and electromechanical parameters obtained as the result of analyzing measured impedance spectra for the fundamental and higher-order resonances of thickness vibrational mode of porous piezoceramics elements.

As can be seen in Fig. 6, the imaginary parts $C^{//}_{33}{}^D$, $C^{//}_{33}{}^E$ parts of elastic moduli of porous piezoceramics increase with the frequency, which is caused by the grows of the ultrasonic

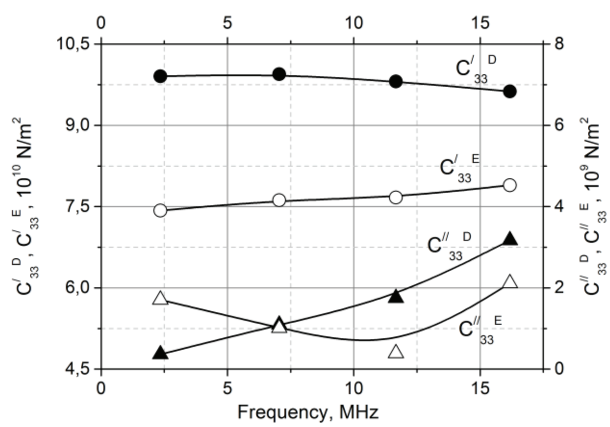

Fig. 6. Frequency dependences of the real $C^{/}_{33}{}^D$, $C^{/}_{33}{}^E$ and imaginary $C^{//}_{33}{}^D$, $C^{//}_{33}{}^E$ parts of elastic moduli of porous piezoceramics $PbTi_{0.41}Zr_{0.49}Nb_{0.057}Zn_{0.0235}W_{0.006}Mn_{0.011}O_3$ + 0.1% GeO_2 with relative porosity 16%.

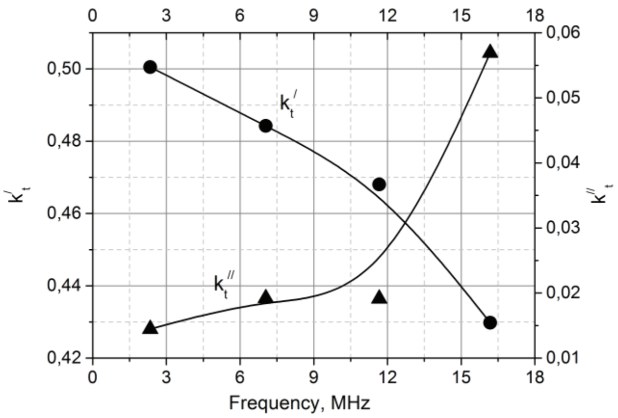

Fig. 7. Frequency dependencies of real $k_t^{/}$ and imaginary $k_t^{//}$ parts of electromechanical coupling factor k_t of porous piezoceramics $PbTi_{0.41}Zr_{0.49}Nb_{0.057}Zn_{0.0235}W_{0.006}Mn_{0.011}O_3$ + 0.1% GeO_2 with relative porosity 16%.

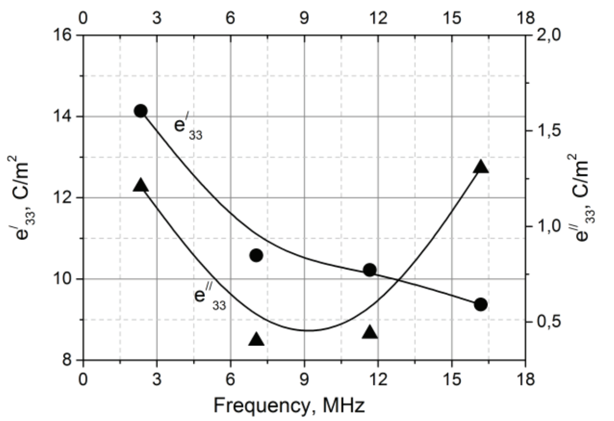

Fig. 8. Frequency dependences of the real $e^{/}_{33}$ and imaginary $e^{//}_{33}$ parts of piezoelectric constant of porous piezoceramics $PbTi_{0.41}Zr_{0.49}Nb_{0.057}Zn_{0.0235}W_{0.006}Mn_{0.011}O_3$ + 0.1% GeO_2 with relative porosity 16%.

waves attenuation as the result of Rayleigh scattering on pores ($\lambda << D$, where λ is the wavelength and D is the average pore size).

In contrast, the real parts of the elastic modulus $C^{/}_{33}{}^{D}$, $C^{/}_{33}{}^{E}$ demonstrate anomalous decrease with frequency grows. We observed such behavior earlier for ferroelectrically "soft" porous piezoceramics and associated it with the frequency dependence of the electromechanical coupling factor k_t for the thickness mode of vibrations, which in particular leads to a decrease in the electromechanical contribution to $C^{/}_{33}{}^{D}$.[15] However, frequency dependencies of complex electromechanical coupling factors as well as piezoelectric constants for porous piezoelectric ceramics have not yet been studied.

Figure 7 shows that the real part of electromechanical coupling factor $k_t^{/}$ of the porous piezoceramics decreases significantly, while the imaginary part $k_t^{//}$ (electromechanical losses) grows rapidly with the frequency which is in good agreement with the frequency dependencies of elastic moduli ($C^{/}_{33}{}^{E} = C^{/}_{33}{}^{D}\,(1 - k_t^2)$) (Fig. 6). The decrease in the electromechanical coupling factor $k_t^{/}$ with the frequency is caused by the strengthening of mechanical clamping of piezoceramics quasi-rod structure in the lateral direction (Figs. 1 and 2).

The real part of piezoelectric constant $e^{/}_{33}$ of porous piezoceramics decreases with the frequency, while imaginary part $e^{//}_{33}$ demonstrate nonlinear frequency dependence (Fig. 8). A number of factors are responsible for the behavior of the piezoelectric constants e_{33} of porous piezoceramics. In the general case, piezoelectric constant of piezoelectric material e_{33} can be written as $e_{33} = d_{33}\,C_{33}^{E} = d_{33}\,C^{/}_{33}{}^{D}\,(1 - k_t^2)$. The fast decrease of the piezoelectric modulus $e^{/}_{33}$ of porous piezoceramics with the frequency grows is caused mainly by the decreased flex-tensional deformations of the branched 3D piezoceramics frame (Figs. 3 and 4) under the influence of external stress (direct piezoelectric effect) or electric field (inverse piezoelectric effect).

In fact, the main physical factor that determines the dispersion characteristics of the complex electromechanical parameters of porous piezoceramics is the scale factor associated with the microstructural features of porous piezoceramics (branched 3D piezoceramics frame structure), which become more pronounced for high-order resonances of thickness vibrational modes.

4. Conclusion

In this work, we studied dispersion characteristics of complex elastic, piezoelectric and electromechanical parameters of ferroelectrically "hard" piezoceramics of the composition $PbTi_{0.41}Zr_{0.49}Nb_{0.057}Zn_{0.0235}W_{0.006}Mn_{0.011}O_3$ + 0.1% GeO_2 with relative porosity 16% and average pore size of 30 μm.

As a result of experimental studies, regions of elastic, piezoelectric and electromechanical dispersion, characterized by anomalies in the frequency dependences of the real and imaginary parts of the complex constants of porous piezoelectric ceramics were revealed. It was found that the main microstructural features of porous piezoceramics that define the character of frequency dependences of complex electromechanical parameters of porous piezoelectric ceramics are branched 3D piezoceramics frame and quasi-rod piezoceramics structure.

It was found out that ferroelectrically "hard" porous piezoceramics are characterized by unique combination of complex electromechanical parameters, that makes it prospective materials for different technical applications.[16–19]

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