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Microstructure characterization and properties of porous piezoceramics

N. A. Shvetsova, I. A. Shvetsov, M. A. Lugovaya, E. I. Petrova and A. N. Rybyanets*
Southern Federal University, No. 194 Stachky Ave, Rostov-on-Don 344090, Russia
*arybyanets@gmail.com

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In this paper, a comprehensive study of microstructure/properties interrelations for porous piezoceramics based on PZT composition was performed. Experimental samples of porous piezoceramics were fabricated using a modified method of burning-out a pore former. Porosity dependencies of elastic, dielectric, piezoelectric and electromechanical coefficients of the porous ceramics in the relative porosity range 0–50% were obtained and analyzed. As a result of microstructure analysis, it was found that at any connectivity type (3–0, 3–3) and porosity up to 50% the real structures of porous piezoceramics were close to the matrix medium structure with continuous piezoceramic skeleton. It was also revealed that the microstructural features of porous piezoceramics define the character of the dependences of the dielectric, piezoelectric and electromechanical properties of porous piezoelectric ceramics on porosity. In conclusion, microstructure/properties interrelations, as well as new applications of porous piezoceramics were discussed.

Keywords: Porous piezoceramics; microstructure; piezoceramic skeleton; electromechanical properties.

1. Introduction

Porous ceramics are heterogeneous media with unique microstructures that provide original, effective properties on which many different applications are based.[1–3] In particular, porous ceramics combine general characteristics associated with the geometry and topology of porous microstructures with the characteristic properties of ceramics as a specific class of materials. It is obvious that the use of porous ceramics is based on the structural and functional properties and characteristics caused by microstructure, the latter being determined by the initial raw material, composition and method of the ceramics fabrication.

Various combinations of basic preparation methods can be used to create hierarchical microstructures with a wide range of pore sizes and/or different pore space topologies at different length scales.[4–6] All of these factors must be considered when selecting the appropriate porous ceramic technology for the microstructure, properties and application requirements.

Intensive R&D and technological works, as well as the development of new manufacturing methods, allowed to organize the mass production of porous piezoceramics with controlled and reproducible porosity and electrophysical properties.[7,8] Porous piezoceramics based on different piezoceramic compositions are widely used now in ultrasonic transducers and sensors for various technical applications.[9,10] However, despite numerous studies, many aspects of the relationship between the microstructure peculiarities and electromechanical parameters of porous piezoceramics are still unclear.

In this paper, a comprehensive study of microstructure/properties interrelation for porous piezoceramics based on PZT composition was performed.

2. Experimental Techniques

Ferroelectrically "soft" PZT-type piezoelectric ceramics of the composition $PbTi_{0.6}Zr_{0.336}W_{0.006}Mn_{0.0233}Nb_{0.0347}O_3$ with different relative porosity in the range of 0–50% and average pore size of 10–30 μm were chosen as the object of the study. Experimental samples of porous piezoceramics were obtained using a modified method of pore formers burning-out.[7] Porosity and pore size distribution were determined using simple but effective methods of stereology and hydrostatic weighing, as well as from the results of weighing and measuring the geometric dimensions of a porous piezoceramics sample, followed by calculation the relative porosity using the formula $p = (p_{\text{theor.}} - p_{\text{exp.}})/p_{\text{theor}}$, where $p_{\text{theor.}}$ is X-ray density of dense piezoceramics and $p_{\text{exp.}}$ is measured density of porous piezoceramics.

Thin discs (diam. 20 mm, thickness 1 mm), rectangular plates (20 × 10 mm, thickness 1 mm) and long rods (diam. 1 mm, length 6 mm) of porous piezoceramics were used for the experiments. Piezoceramic elements were polarized in air by applying to vacuum evaporated Cr/Ni electrodes dc electric field (~ 1 kV/mm) at heating above Curie temperature (~340 °C) and cooling to a room temperature.

Microstructural studies were performed on polished and chipped surfaces of porous piezoceramics samples using

*Corresponding author.

the scanning electron microscopes (JEOL JSM-6390LA and TM-100, Hitachi).

Piezoresonance spectra measurements for radial, length-extensional and thickness modes of vibrations were made using Agilent 4294A impedance analyzer. The measurements were carried out in accordance with the IEEE Standard[11] on samples of porous piezoceramics obtained using the same technological regimes.

Porosity dependencies of dielectric, piezoelectric and electromechanical coefficients of the porous ceramics in the relative porosity range 0–50% were obtained as the result of analyses of measured piezoresonance spectra.

3. Results and Discussion

3.1. *Microstructure study*

Micrographs illustrating the main features of the porous piezoceramics microstructure are shown in Figs. 1–4. According to the images, the porous piezoceramics are characterized by random distribution of irregular shape pores (dark spots in the gray piezoceramics matrix) with the average size of 10–30 μm.

With an increase in porosity, the appearance of larger branched pores formed as a result of the coalescence of neighboring smaller pores is observed. We also noticed that at low porosity, the pores are mostly isolated, while at higher porosity, the pores are interconnected.

The case of isolated pores corresponds to 3–0 connectivity while the interconnected pores case corresponds to 3–3 connectivity.[12] It can be seen from the micrographs that the ceramic skeleton is characterized by dense packing of grains with average size 3–5 μm that does not differ from the grain size observed for dense piezoceramics of the same composition.

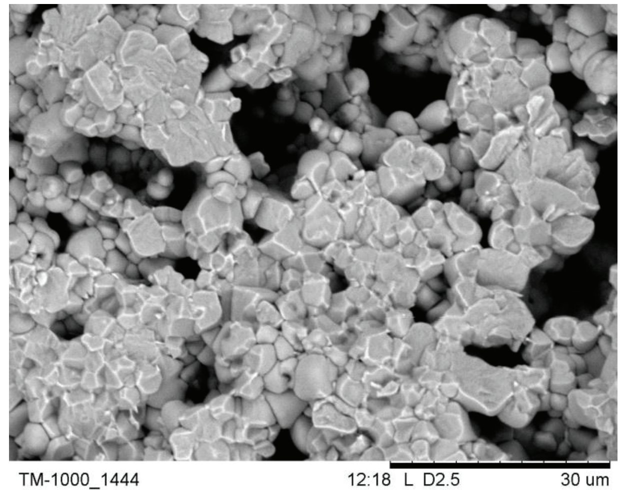

Fig. 2. Microstructure of the porous piezoceramics with the relative porosity 29%.

These micrographs demonstrate also the presence in porous piezoceramics of a rigid three-dimensional (3D) piezoceramics skeleton with continuous quasi-rod structure. The branched coral-type microstructure of porous ceramics determines the main features of its electromechanical properties.

3.2. *Electromechanical properties study*

Figures 5–7 show the dependences of the main electromechanical parameters of the studied porous piezoceramics on the relative porosity.

The dielectric constant of porous piezoceramics $\varepsilon_{33}{}^{T}/\varepsilon_0$ decreases almost linearly when porosity grows (Fig. 5),

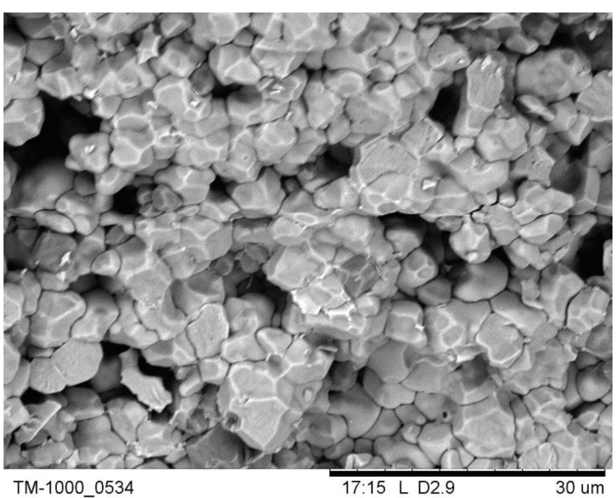

Fig. 1. SEM image of chipped surface of the porous piezoceramics with the relative porosity 21%.

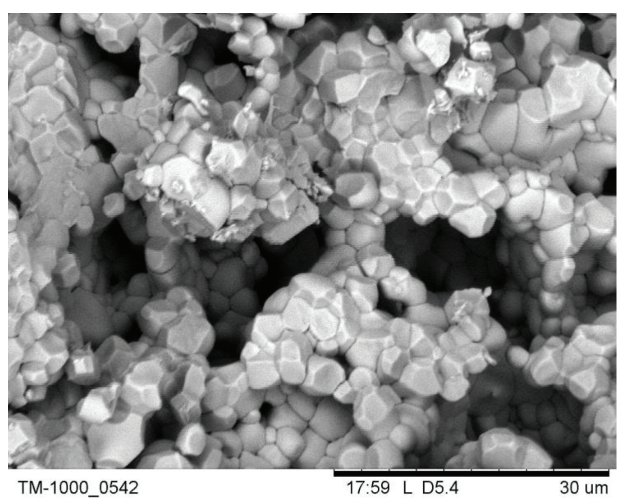

Fig. 3. Microstructure of the porous piezoceramics with the relative porosity 41%.

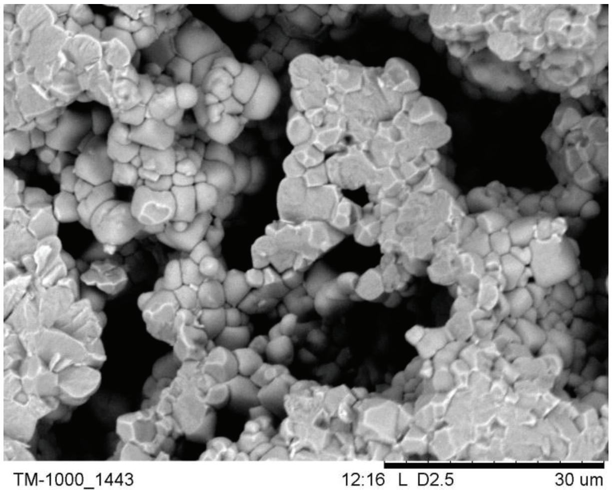

Fig. 4. Microstructure of the porous piezoceramics with the relative porosity 49%.

which is due to a significant difference in the dielectric constants of piezoelectric ceramics and air.

The dielectric loss tangent tgδ decreases slightly with porosity increase in the entire range of porosity values (Fig. 5) and approaches the initial value only at p ~ 0.5. A more developed internal surface of the porous piezoceramics contributes to the fixation of domain walls and leads to decrease in tgδ.[8]

It should be noted that highly porous piezoceramics are hygroscopic, and correct measurements must be carried out at a controlled atmospheric humidity.

An increase in porosity p leads to noticeable changes in the piezoelectric moduli d_{33} and d_{31} of the porous piezoceramics (Fig. 6). A number of factors are responsible for the behavior of the piezoelectric moduli of porous piezoceramics.

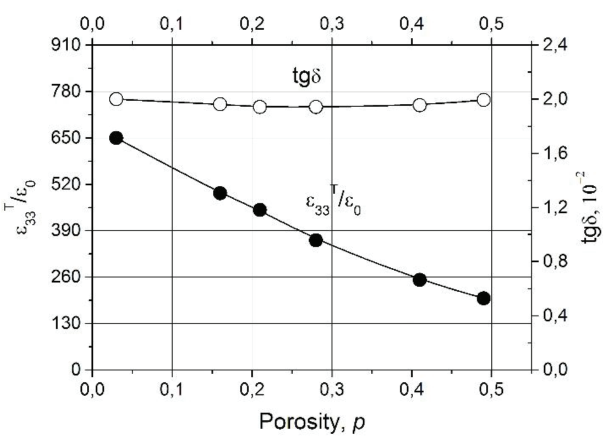

Fig. 5. Dependences of the dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and the loss tangent tgδ on the relative porosity p for porous piezoceramics of the composition $PbTi_{0.6}Zr_{0.336}W_{0.006}Mn_{0.0233}Nb_{0.0347}O_3$.

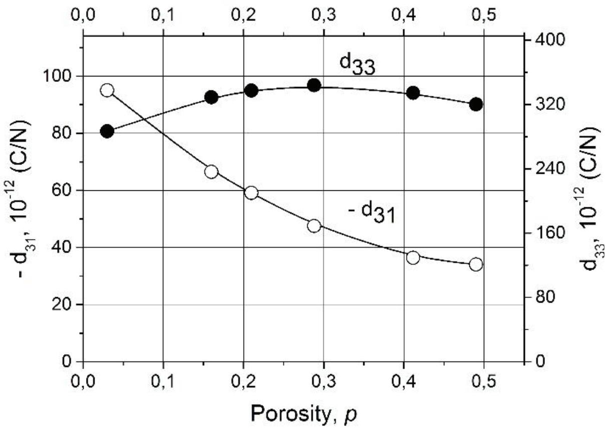

Fig. 6. Piezoelectric modules d_{33} and $(-d_{31})$ as function of the relative porosity p for porous piezoceramics of the composition $PbTi_{0.6}Zr_{0.336}W_{0.006}Mn_{0.0233}Nb_{0.0347}O_3$.

The formation of continuous quasi-rod structure of porous piezoceramic in the direction of remnant polarization (Figs. 3 and 4) ensures the constancy of the piezoelectric modulus with porosity grows. A decrease in the surface area of the piezoelectric active phase is balanced by an increase in the specific pressure on the piezoceramics skeleton.

The growth of the piezoelectric modulus d_{33} of porous piezoceramics with the porosity is caused by the increased flex-tensional deformations of the branched 3D piezoceramics skeleton (Figs. 3 and 4) under the influence of external stress (direct piezoelectric effect) or electric field (inverse piezoelectric effect).

Fast decrease in $|d_{31}|$ of porous ceramics with porosity grows (Fig. 6) is caused by the breach of the electromechanical connectivity of the nonuniformly polarized piezoceramics skeleton in the direction of remnant polarization and in the lateral directions.

The decrease in the electromechanical coupling factor k_{33} for length-extensional mode of vibration for piezoceramics rod with porosity grows (Fig. 7) is caused by a rapid increase in the elastic compliance S_{33}^E of the porous piezoceramics skeleton ($k_{33}^2 = d_{33}^2/(\varepsilon_{33}^T S_{33}^E)$). A further decrease in k_{33} is prevented by the weakening of the mechanical clamping of the piezoceramics skeleton in the lateral direction as result of the formation of a branched quasi-rod structure (Figs. 3–5).

The behavior of electromechanical coupling factor k_p for radial vibrational mode of thin piezoceramics disk at porosity grows (Fig. 7) is determined by competing influence of decrease in piezomodulus d_{31} and dielectric permittivity ε_{33}^T, and fast increase of elastic compliances S_{11}^E and S_{12}^E according to following relation: $k_p^{2*} = 2d_{31}^{*2}/(\varepsilon_{33}^{T*}(S_{11}^{E*} + S_{12}^{E*}))$. The main reason of k_p decrease is the above-mentioned breach of the electromechanical connectivity of the piezoceramic skeleton in the lateral direction and fast increase in corresponding elastic compliances of porous ceramics.

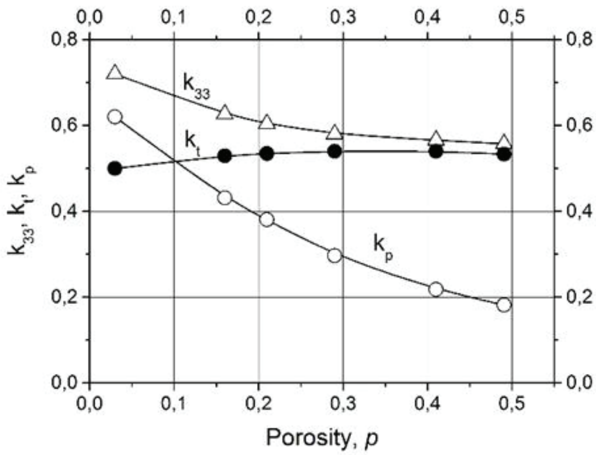

Fig. 7. Electromechanical coupling factors k_{33}, k_t and k_p as function of the relative porosity p for porous piezoceramics of the composition $PbTi_{0.6}Zr_{0.336}W_{0.006}Mn_{0.0233}Nb_{0.0347}O_3$.

Significant increase in the electromechanical coupling factor k_t for thickness vibrational mode of thin piezoceramics disk at porosity grows (Fig. 7) and its approach to the longitudinal electromechanical coupling factor k_{33}, is caused by the partial removal of the mechanical clamping of the quasi-rod piezoceramics skeleton in lateral direction, which is typical for dense piezoceramics.

The relationship between the resulting values of the considered electromechanical coupling coefficients at any porosity is well described by an approximate relation: $k_t^2 \approx (k_{33}^2 + k_p^2)/(1 - k_p^2)$.

4. Conclusion

As a result of SEM microstructure analysis, it was found that at any connectivity type (3–0, 3–3) and porosity up to 50% the real structures of porous piezoceramics were close to the matrix medium structure with continuous coral-like piezoceramic skeleton.

It was revealed that the following microstructural features of porous piezoceramics define the dielectric, piezoelectric and electromechanical properties of porous piezoelectric ceramics-branched flexible 3D piezoceramics skeleton and quasi-rod piezoceramics structure in the direction of residual polarization of porous piezoceramics.

Changes in the mechanical and electrical boundary conditions on the branched coral-like microstructure, as well as inhomogeneous polarization of the piezoceramic skeleton also play a significant role in the formation of electromechanical properties of porous piezoelectric ceramics.

It was found out that porous piezoceramics similarly to 1–3 type composites are characterized by increased values of k_t and d_{33}, and reduced values of d_{31}, k_p, compared to dense piezoceramics, that makes it perspective materials for different ultrasonic applications in medical diagnostics and therapy, nondestructive testing, and active piezoelectric membranes for reverse osmosis, ultrafiltration and microfiltration processes.[13–15]

Acknowledgments

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