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Surface modification and preservation of bulk properties of piezoelectric ceramics under the exposure to hydrogen plasma flow.

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Experimental results of pulsed hydrogen plasma impact on piezoelectric ceramics on the example of domestic composition CTSNV-1 are presented. Significant changes in the elemental composition and surface topography were revealed with a characteristic depth of the modified layer of the order of $20\,\mu$m. The study of piezoelectric properties of CTSNV-1 after exposure to hydrogen plasma (integral particle flux to $\sim 10^{23}\,\mathrm{m}^{-2}$, energy $\sim 100\,$eV) showed a decrease in the electromechanical coupling coefficient of the thickness mode k_t samples (from ~ 0.6 to ~ 0.3) while keeping the piezoelectric constant values d_{33} within $450 \pm 50\,$pm/V and dielectric constant ε_{33} within 2250 ± 560, which corresponds to the manufacturer's data on the spread of these values for standard samples.

Keywords: piezoelectric ceramics, hydrogen plasma, surface morphology, piezoelectric constant, electromechanical coupling coefficient.

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Piezoelectric ceramics is widely used for ultrasonic piezoelectric transducers, including those for nondestructive testing, sensors of various physical parameters, and as a material for the manufacture of precision piezoelectric drives (actuators) [1]. The use of the above devices implies their correct functioning in various extreme conditions. In recent years, the prospects of using piezoelectric elements as part of diagnostic and protective equipment in nuclear fusion reactors have aroused great interest. One of such elements is a piezoelectric motor being developed at the A.F. Ioffe Institute of Physics and Technology for the International Thermonuclear Experimental Reactor (ITER), in which the possibility of using piezoceramics based on lead zirconate-titanate $PbZr_{1-x}Ti_xO_3$ (LZT) [2] is being considered. Successful solution of such a problem necessitates the development of experimental methods to study the stability of piezoelectric materials parameters to the impact of plasma of different composition, density and energy of particles, as well as to analyze the possibilities of restoring the operating characteristics of devices based on them.

To date, the most studied material for the inner surface of nuclear fusion reactors is tungsten due to its good thermal conductivity and high melting point. However, it is known to suffer from bombardment by hydrogen and helium isotopes whose energies range from 10 eV to a few keV [3]. It has been experimentally established that repeated exposure of tungsten to hydrogen, deuterium and helium plasma causes significant modification of the near-surface layers in the form of bubbles, bloating and flaking [3–8]. This can lead to decreased thermal conductivity [4], increased stiffness, and consequent brittleness of the material [7], which is a serious problem in the design, as well as for the subsequent stable and safe operation of nuclear fusion plants. It should be noted that experimental studies and analysis of the processes initiated by the influence of plasma on piezoceramic materials, their development under prolonged plasma exposure and interrelation with the main physical parameters of piezoceramics are at the very initial stage. The present work presents the first experimental results of the study of surface modification and its relationship with the change in bulk piezoelectric properties of samples of domestic piezoelectric ceramics CTSNV-1 („Aurora-Elma", Volgograd, avrora-elma.ru) under the exposure to a hydrogen plasma jet. The samples for the studies were cut from a standard polarized disk with a diameter of 6 cm and thickness ~ 3 mm, had a surface area (perpendicular to the polarization direction) $\sim 1\,\mathrm{cm}^2$. The fired silver electrodes were removed from surface of the samples. Measurements of capacitance (and consequently dielectric permittivity), piezoelectric constants and electromechanical coupling coefficients of the prepared samples were carried out after application of conductive silver paste (drying without high-temperature annealing) to ensure the uniformity of measurement conditions performed before and after plasma exposure.

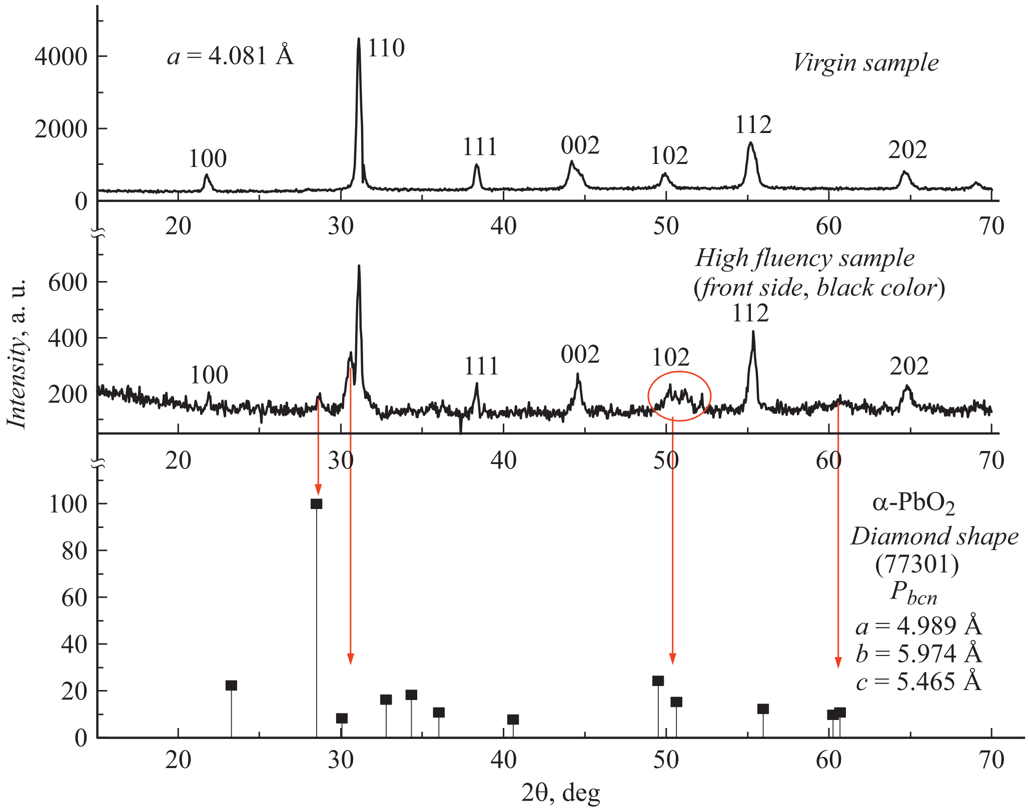


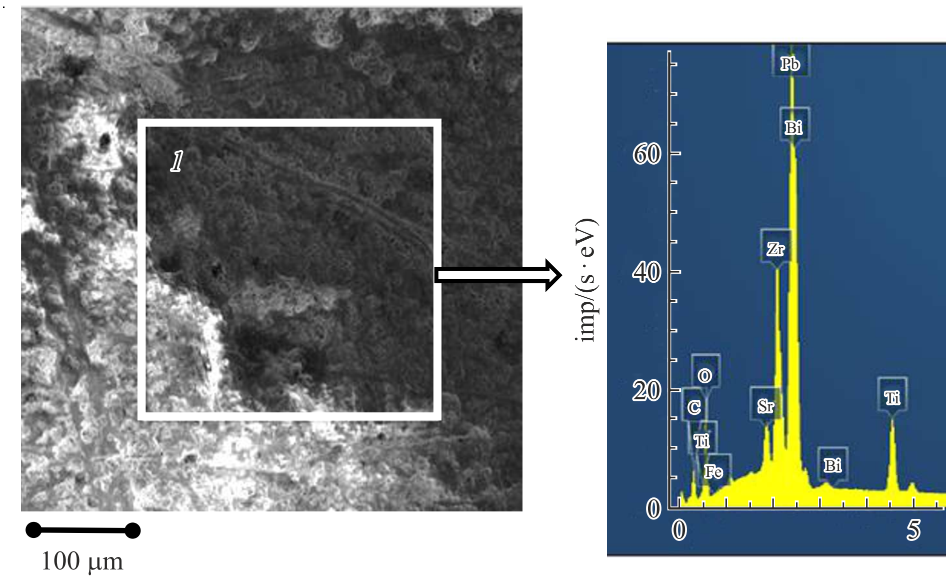
Figure 1. Diffraction patterns of CTSNV-1 piezoceramic samples before (*Virgin sample*) and after (*High fluency sample*) exposure to a hydrogen plasma jet. A bar diagram of lead dioxide in the form α-PbO_2 from the JCPDS X-ray file is shown below.

The samples were irradiated on the plasma gun bench, which allows simulating cyclic exposure to ITER plasma with different composition of the working gas and the possibility to vary the intensity of exposure [9]. To measure plasma jet parameters, the bench is equipped with a set of necessary diagnostic devices. In the experiments, hydrogen was used as the working gas. The configuration of the setup allowed the formation of a plasma jet of diameter $\sim 4-5$ cm with energy up to 175 J. The plasma pulse duration was $\sim 20\,\mu$s at an ionization front velocity of more than 100 km/s. The calculated value of particle fluence on samples of area 1 cm^2 was $\sim 6 \cdot 10^{21}$ m^{-2} (particle energy within 100–200 eV) per pulse. In the experiment, samples exposed to 20 plasma pulses while they were placed at different distances from the source were studied. The average pressure on the surface of the test sample mounted at a minimum distance from the source equal to 30 cm („strong exposure") is ~ 0.15 MPa, the calculated value of temperature on the surface of the sample is $\sim 800^\circ$C. At a distance of 100 cm from the source („weak exposure") the jet pressure decreases by an order of magnitude, the calculated value of the temperature on the target surface is $\sim 400^\circ$C. Initial visual inspection of the samples after irradiation showed a significant change in the surface color of the samples on the exposure side: from dark gray for the samples after „weak exposure" to almost black as a result of „strong exposure". This effect can be attributed to the formation of lead oxides on the surface, in particular lead oxide Pb_2O (amorphous material or black cubic crystals) or lead dioxide in the form α-PbO_2 (black crystals of rhombic crystal system). The formation of the above oxides is possible at heating of lead, which is a part of LZT-ceramics, to temperatures on the order of 300°C without access to air, which quite corresponds to the conditions of the experiment in the plasma gun.

The surface structure of the samples was analyzed on an X-ray diffractometer DRON-3 (CuK_α-radiation, tube voltage 38 kV, current 18 mA). The diffraction patterns of CTSNV-1 piezoceramic samples before and after irradiation are shown in Fig. 1.

The results of the study showed that even after „a strong exposure" the sample as a whole retains a single-phase structure and has no signs of amorphization (structure parameters were calculated in the pseudocube approximation). At the same time, in Fig. 1 (middle fragment) the reflexes not belonging to the structure of the tetragonal phase of CTSNV-1 are observed. The presence of such features correlates well with the assumption of the occurrence of lead dioxide crystals in the form of rhombic α-PbO_2 (bottom fragment in Fig. 1) having visually black coloration on the surface of piezoceramics.

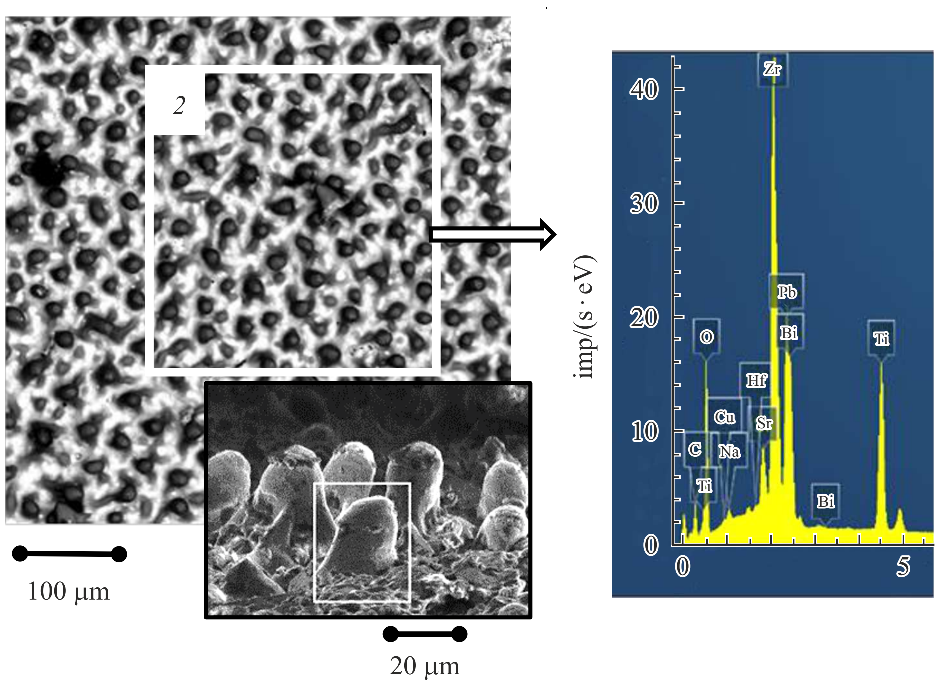
Experimental studies of the ceramic surface before and after plasma exposure were also performed using scanning electron microscopy (SEM) on TESCAN MIRA (TESCAN, *a*



Spectrum 1

Element	wt.%
Pb	53.9
O	17.8
Zr	14.8
Ti	6.2
Bi	6.0
Sr	1.2
Fe	0.1

b



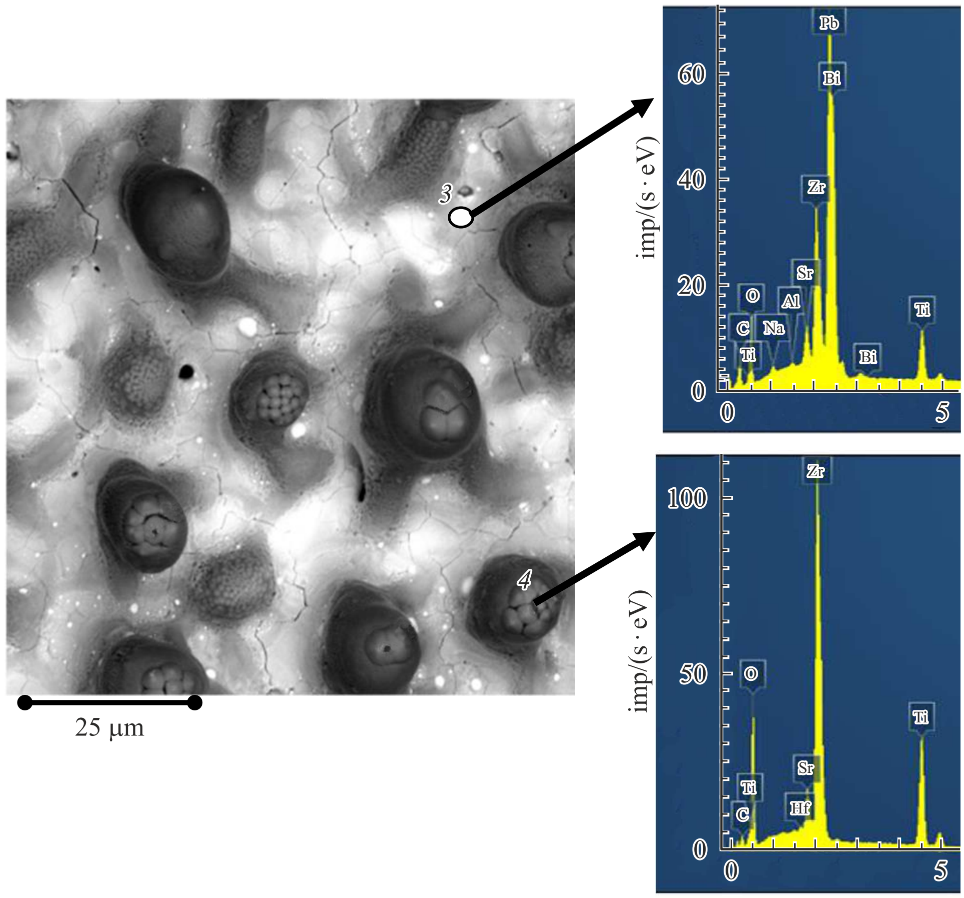
Spectrum 2

Element	wt.%
Zr	28.5
O	27.6
Pb	26
Ti	11.4
Bi	2.8
Sr	2.1
Hf	0.8
Na	0.6

Figure 2. SEM images of the surface of CTSNV-1 piezoceramic samples before (*a*) and after (*b*) multiple (20 pulses, „strong exposure") irradiation with hydrogen plasma flow. Beam parameters: single pulse duration $\sim 20\,\mu$s, particle energy ~ 100 eV, integral fluence $\sim 10^{23}\,\mathrm{m}^{-2}$.

Czech Republic) and JSM 7001F (JEOL, Japan) equipment in the secondary electron mode at an accelerating voltage of 5 keV and a beam current of about 20 pA. The surface microstructure of the unirradiated and irradiated CTSNV-1 piezoceramic samples are shown in Fig. 2, *a* and *b*, respectively.

The images in Fig. 2 show that a pronounced relief in the form of „hills" with a rounded top and characteristic dimensions of diameter and height on the order of $10-20\,\mu$m was formed on the surface of the irradiated sample. This relief may be due to the melting in the near-surface layer of lead — a fusible component of the LZT-ceramic solid solution — with its subsequent release to the surface and evaporation. Carried on a solid surface melt jets have a weak thermal contact and poor adhesion with the surface, which when exposed to plasma can contribute to the flight of droplets and start the process of droplet erosion, observed earlier at prolonged plasma irradiation of tungsten, titanium, iron and other metals in helium plasma discharges [10]. As shown by elemental analysis of the surface composition of



Spectrum 3

Element	wt.%
Pb	56.8
O	15.4
Zr	14.3
Bi	6.4
Ti	5.4
Sr	0.9
Na	0.5

Spectrum 4

Element	wt.%
O	42.8
Zr	41.7
Ti	12.4
Sr	2.1
Hf	0.3

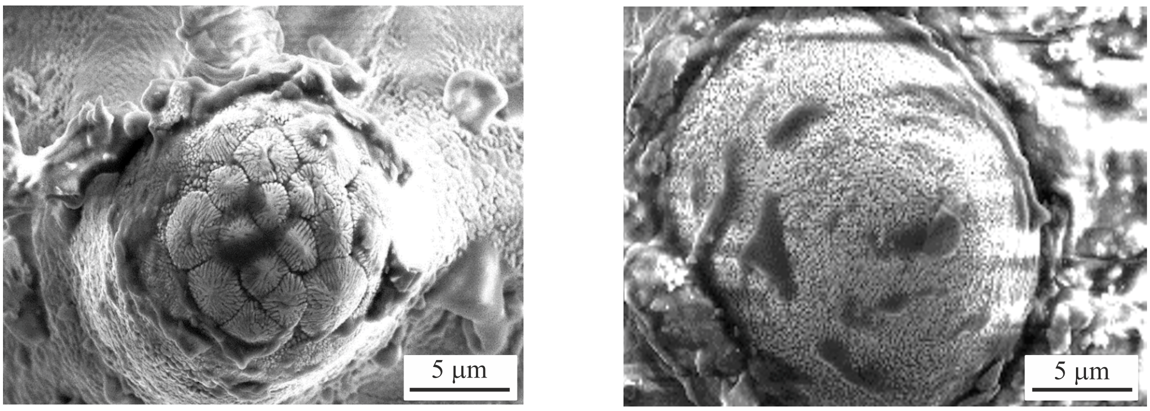


Figure 3. Surface microstructure of a piezoceramic sample after multiple irradiation with hydrogen plasma flow.

the „heavily irradiated„ sample using SEM, a decrease in the percentage of lead is observed in it by more than a factor of 2 (Fig. 2).

More detailed SEM images of the structure of „hills“ on the surface of the irradiated ceramic sample are presented in Fig. 3. As can be seen from the figure, the surface has formed a relief with micro- and nanostructures consisting of „hills“ or „bubbles“ at different stages of evolution. At the tops of these formations, one can observe structures resembling highly porous regions with a "cauliflower" type structure with characteristic dimensions on the order of 200 nm, similar to those found earlier under prolonged plasma loads on the surfaces of reactor inner chamber regions made of various structural materials (tungsten, steel, titanium, and other metals) [8].

The sample after „strong exposure“ showed a significantly heterogeneous nature of elemental composition on its surface: the composition of the light region between the„hills“ (spectrum *3* in Fig. 3) corresponds to the composition of the unexposed sample (spectrum *1* in Fig. 2); a fibrous structure is observed on the surface of the hills, in the composition of which lead is completely absent (spectrum *4* in Fig. 3).

Obviously, the observed surface modification of the piezoceramic sample depends on its composition and should affect the change of its physical characteristics, primarily related to thermal, elastic and electromechanical properties, which undoubtedly requires further research. However, at this stage, the main purpose of the experiments was to study the effect of the proposed surface modification of the samples on their bulk physical parameters related to polarization: piezoelectric constant d_{33} and electromechanical coupling coefficient k_t. To measure d_{33}, we used both the static method of recording the change in sample thickness in the direction of electric polarization under the action of the applied voltage (inverse piezo effect) and the pulse [11] method implemented on the basis of an ultrasonic echo-pulse unit and a piezoelectric transducer with a delay line operating in the MHz frequency range (direct piezo effect). Measurements of the responses of the unexposed sample and samples subjected to „weak„ and „strong „ exposures showed no change in their behavior, indicating that the bulk polarization of the samples was preserved.

The electromechanical coupling coefficient k_t is one of the most important characteristics of piezoelectric materials, reflecting the efficiency of converting electrical energy into mechanical energy and vice versa. Piezoceramics of LZT composition have high conversion efficiency. For the CTSNV-1 samples investigated in this work, the value of the electromechanical coupling coefficient is one of the highest among all known for commercially available piezoelectric materials and can reach values ~ 0.6 [1]. The electromechanical coupling coefficient of the thickness mode of oscillations k_t was calculated from the results of experimental measurement of the electromechanical resonance spectra of the sample oscillating perpendicular to the surface (thickness mode) using the method of non-equidistance of frequencies of higher odd harmonics [12]. The measured values of the electromechanical coupling coefficient of the thickness mode of oscillations in the unexposed sample were $k_t = 0.58$, for the sample subjected to „weak exposure“, its value decreased to $k_t = 0.27$, but in the sample after „strong exposure“ the coefficient k_t not decreased, but showed an increasing trend: $k_t = 0.32$. The most probable reason for the decrease in the electromechanical coupling coefficient is modification of the surface layer and associated defects (dislocations) in the near-surface region of the sample. This is also evidenced by the change in the magnitude of the dielectric loss angle tangent, which also shows a sharp increase for the sample under „weak exposure“: increases by a factor of 3.7 from $\mathrm{tg}\,\delta = 0.0087$ for the unexposed sample to $\mathrm{tg}\,\delta \approx 0.0318$ for the exposed sample. Interestingly, in the sample after „strong exposure“ is observed some „recovery“ of the dielectric loss angle tangent to $\mathrm{tg}\,\delta \approx 0.0027$, which corresponds to its decrease by a factor of only 3 compared to the value for the unexposed sample. The latter result allows us to hope that under certain conditions in piezoelectric materials under the exposure to plasma can start self-repair mechanisms, but to understand the nature of this phenomenon we need additional experimental studies.

The main result of the work is the experimental confirmation of electric polarization preservation and insignificant decrease of the main electrophysical parameters of piezoelectric ceramics CTSNV-1 even under very strong exposures to hydrogen plasma jet with energy 175 J, creating on the surface of samples the pressure up to 0.15 MPa and temperature up to 800°C. The piezo coefficient d_{33} retains its value in the range 450 ± 50 pm/V, the electromechanical coupling coefficient k_t decreases approximately by a factor of 2, showing a tendency to recover with increasing plasma intensity. A similar process is observed for the dissipation factor, although its value increases by a factor of about 3 compared to the value for the unexposed sample.

The results obtained are important both for practical applications and for fundamental understanding of the properties of ferroelectric materials and the processes occurring in them under various external extreme influences.

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Conflict of interest

The authors declare that they have no conflict of interest.

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