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Effect of neutron and gamma radiation on the interface electrode-piezoceramics

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Synthesized ceramics of the composition $0.64BiScO_3-0.36PbTiO_3$ with deposited gold electrodes were subjected to irradiation with fast neutrons and gamma rays with a fluence of $\sim 5\cdot 10^{19}$ n/cm^2(γ/cm^2) at an energy $E > 0.1$ MeV. The elemental composition of the electrode and the electrode-ceramics interface, as well as the crystal structure of the interface after irradiation, were studied. The experimental results indicate a significant effect of irradiation on the gold electrode and the crystal structure of the interface.

Keywords: piezoelectric ceramics, radiation resistance, electrode-piezoceramics interface.

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1. Introduction

Piezoelectric ceramics is the base material used in manufacturing of piezoelectric transducers, electromechanical drives (actuators) and sensors of various physical quantities. Piezoceramics-based instruments, devices and complex measuring and diagnostic systems are widely used in various industries, such as the automotive, petrochemical, iron and steel industries, nuclear power and the aerospace industry [1–4]. Metallization is an absolute prerequisite for piezoceramic element applications. The electrode material depends on the chemical composition of a piezoceramic element, device design and operating conditions. Along with silver (Ag) electrodes widely used in industrial production of bulk active elements [5,6], platinum (Pt), nickel (Ni), copper (Cu), an silver (Ag) palladium (Pd) alloy are used for thick films and multilayer ceramic actuators [7].

When developing instruments capable of operating at elevated temperatures, high-temperature piezoceramics, including $0.64BiScO_3-0.36PbTiO_3$(BSPT) solid solution, are of particular interest. The use of such ceramics makes it possible to expand the range of operating temperatures from 150°C, typical for lead zirconate titanate (PZT) piezoceramics, to 300°C, taking into account the Curie temperature for the BSPT composition $T_c \approx 450$°C and rather high piezoelectric coefficients [8–12]. Operation of piezoelectric motor power components [13] developed under the International Thermonuclear Experimental Reactor (ITER) project, implies the operating temperature range up to 300°C. The ITER project is intended to demonstrate the deuterium-tritium (D-T) reactor operation, commercial applicability of the thermonuclear reaction and to solve numerous physical, physicochemical and technological problems. Piezomotors using active piezoceramic elements shall function as part of optical diagnostic systems during implementation of the ITER project and maintain their performance in intense neutron and gamma ray fluxes (fluence $\sim 10^{19}$ n/cm^2, energy $E > 0.1$ MeV) [13,14]. Our study has shown that, besides the extended temperature range and acceptable piezoelectric coefficients, BSPT ceramics exhibits radiation resistance of both elemental composition and crystal structure at neutron flux fluence $\sim 10^{19}$ n/cm^2, $E > 0.1$ MeV [15]. It should be noted that when piezoceramic products are used in a reactor, not only the ceramics, but also the electrode material necessary for the piezoelectric active element operation are exposed to radiation. Variation of the near-electrode layer (electrode-ceramics interface) properties after irradiation is of particular importance, because the interface might have a significant effect on the dielectric and piezoelectric responses of the sample when an external electric field is applied.

Currently, no information is available in literature about possible silver corrosion under the expected ITER conditions. However, there is data on silver corrosion in gases (including oxygen), in the presence of sulfur, at high temperatures, as well as on the influence of electrocorrosion that occurs under the influence of current from external sources [16,17]. Moreover, simulation and analysis of possible accidents during ITER operation showed that loss-of-coolant (water) accident may result in water steam appearance in the piezo motor area (in the ITER diverter) [18], and, accordingly, to changes in electrode characteristics. It is known that according to corrosion resistance decrement the remaining noble metals form the following series: iridium, ruthenium, rhodium, gold, platinum, palladium [16]. Thus,

for example, gold (Au) electrodes can be used as an alternative to Ag electrodes. Taking into account the harsh operating conditions (high-intensity neutron and gamma fluxes, and thermal loads) of active piezoelectric elements, the purpose of this study is to investigate the effect of neutron and gamma radiation on the Au electrode–BSPT piezoceramics interface.

2. Experiment

Ceramic samples of $0.64BiScO_3-0.36PbTiO_3$ solid solution were prepared using conventional ceramic processing technique. The resulting powder after calcination was pressed into disks with a diameter of 10 mm and a thickness of 1.5−2 mm at 8 MPa. The samples were finally sintered at 1100°C for 2 h. Loss of PbO by weight was less than 1%. For details of ceramics synthesis see [15]. Study of the prepared samples was carried out, including X-ray diffraction examination (DRON-3 diffractometer, scanning in 2θ range from 10 to 60° at 0.1 increments) and elemental analysis of ceramics (scanning electron microscope with TescanMira elemental analysis system). The density of the samples was 93−96% of the theoretical X-ray density. The samples were of single-phase type. The magnetron sputtering method was chosen to form gold electrodes, because it ensures high deposition rate of the sputtered material. Gold electrode were sputtered on ceramics using Cressington 108 AUTO system. A chromium sublayer was preliminary applied to the sample surfaces. Measurements carried out using BV-7669 profilometer showed that the thickness of the resulting electrode with chromium sublayer was 1 μm. Samples with deposited gold electrodes were exposed to radiation close to the spectrum expected in ITER. The total irradiation fluence was $\sim 5 \cdot 10^{19}$ n/cm^2 ($E > 0.1$ MeV). The sample temperature during irradiation was about 200°C. For details of radiation testing of ceramics with electrodes see [15].

3. Results and discussion

After irradiation, not only the BSPT ceramics [15], but also the gold electrode and the electrode-ceramics interface were examined. Elemental composition measurements of the electrode after irradiation, both in the electrode area of 0.96 mm^2 (Figure 1), and in a local area of $6.4 \cdot 10^{-5}$ mm^2, which corresponds to the mean grain size of ceramics $\sim 10\,\mu$m (Figure 2), show a decrease in the gold content on the electrode surface from initial 100% to 54% and 59%, respectively.

Modification of the gold electrode is also confirmed by darkening of the electrode after irradiation.

The presence of aluminum and silicon in the electrode spectra (Figure 1, 2) may be explained by the effect of the aluminum flask material, in which the ceramic samples were immersed into the nuclear reactor pool [15]. For example, $^{27}Al + {}^1n \rightarrow {}^{28}Al$ (neutron capture) reaction followed by decay $^{28}Al \rightarrow {}^{28}Si + \beta$ (β-decay, half-life 2.24 min) is possible and results in the appearance of silicon recoil nuclei with ~ 500 eV. Such silicon atoms, escaping from the inner surface of the aluminum ampoule, can be absorbed in the upper layer of the gold electrodes, stimulating additional diffusion of Au atoms from the electrode surface into the near-electrode layer.

The resulting spectra show the radiation-induced diffusion of gold into ceramics and of lead to the sample surface. The possibility of radiation-stimulated diffusion as a result of the irradiation-induced formation of defects (vacancies and interstitial atoms) was originally predicted for semiconductors [19]. A special focus is currently made on irradiation-induced processes in heterogeneous systems, including the metal contact-material interface, due to the extensive use of radiation for modification of materials properties. In such systems, along with diffusion of metal atoms into the material during irradiation, introduction of material atoms into the electrode can be also observed. These processes were commonly named „ion-beam mixing“ [20]. A possible mechanism for such processes is the formation of interstitial-vacancy pairs and interstitial atoms in the material. As a result, there is a radiative decrease in the thermal diffusion activation energy both within the ceramics and at the ceramics-metal interface resulting in counter diffusion [21].

In our case, we can assume that counter processes occur: diffusion of gold into the ceramics and diffusion of piezoceramics elements to the gold electrode induced by irradiation with neutrons and gamma-quanta. Modification of the electrode is observed in the experiment, as noted above, in the form of a decrease in gold content in the electrode and in the appearance of ceramics elements such as Pb, Bi, Ti, Sc and O in the electrode. The irradiation-induced increase in the content of these elements in the near-surface ceramics layer compared with the content within the ceramics was recorded by us in [15]. The process behavior depends, first of all, on the release of lead oxide and bismuth oxide from within the material to the surface after irradiation, similar to the evaporation processes of these oxides during the ceramics synthesis and at high temperatures [22], and on less pronounced diffusion of Ti and Sc into the electrode material. The detailed description of the radiation-induced diffusion processes in this system requires additional study.

To study the properties of the interface after neutron irradiation, the gold electrodes were removed from the sample surfaces by „aqua regia“ etching. For comparison, a similar virgin ceramics sample was etched. In contrast to the non-irradiated sample, on which the gold electrodes dissolved in aqua regia within 2 min, this process for the irradiated samples took 2 h, which is explained by the gold diffusion into the piezoceramics surface layer. It should be noted that a white coating occurs on the sample surfaces after etching. elemental composition examination of the white coating of the sample using an electron microscope (penetration distance of about 1 μm) showed that it consists mainly of $PbCl_2$. Lead chloride is obtained as a result of the

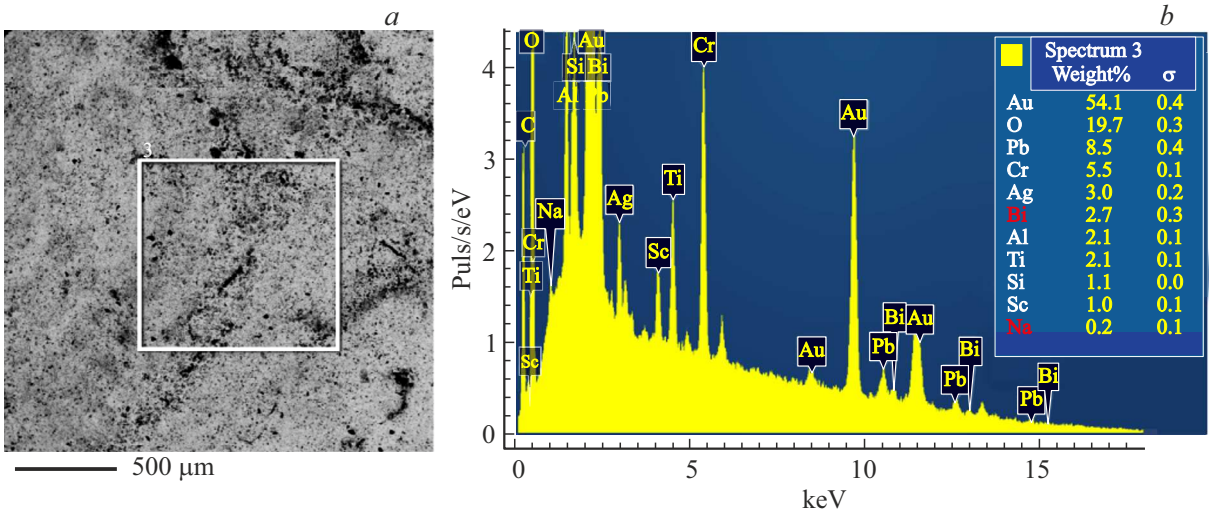

Figure 1. Electronic image of a gold electrode surface area after irradiation (a) and spectrum reflecting the elemental composition of the electrode (b).

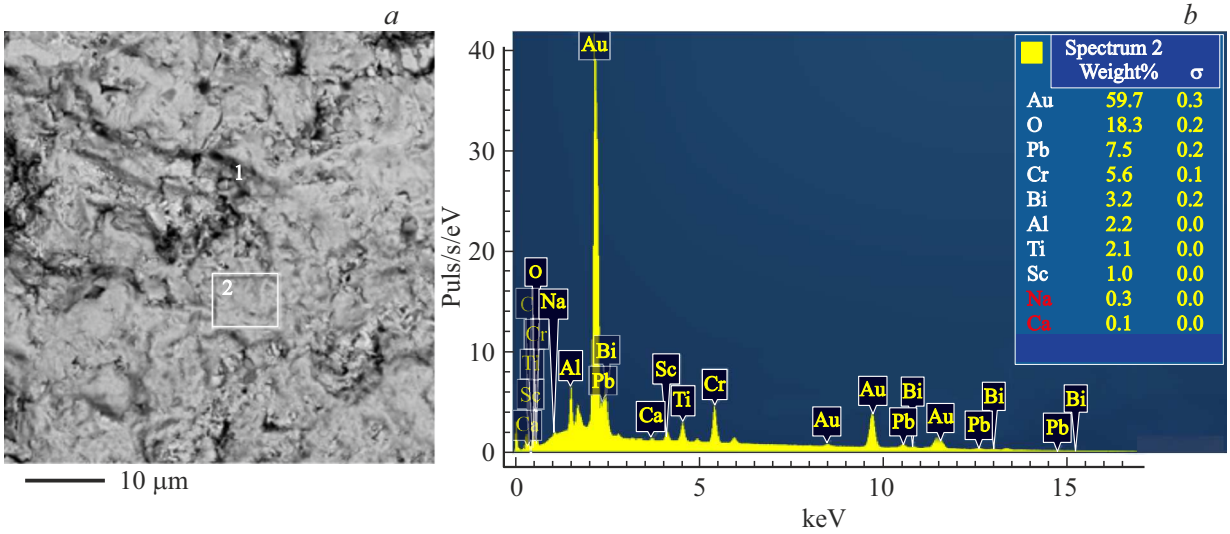

Figure 2. Detailed electronic image of the electrode surface area (2) after irradiation (a) and the spectrum reflecting the elemental composition of the electrode in this area (b).

interaction of lead ions as part of the ceramics with an active oxidizing agent, chlorine, formed by the interaction of nitric and hydrochloric acids as part of aqua regia (Figure 3).

At the final stage, the white coating ($PbCl_2$) was completely removed by the sample treatment in an ultrasonic bath for 5 min. X-ray diffraction analysis of the near-electrode layer of the irradiated sample after removal of the electrode and white coating (radiation penetration distance of about $10\,\mu$m) showed that the crystalline structure of the layer inherent in the bulk sample after irradiation was preserved (Figure 4, a). Comparison of Figure 4, a and b shows that the X-ray spectra are qualitatively similar. However, if an anisotropic radiation-induced alteration of the lattice occurs within the sample with an increase in tetragonality ($c/a = 1.026$) by 0.47% compared with the non-irradiated sample, then radiation-induced expansion of the crystal lattice occurs in the near-electrode layer followed by anisotropic increase in parameters and decrease in tetragonality to $c/a = 1.024$. Thus, $a = 4.012 \pm 0.003$ Å (a of the irradiated sample without electrodes is equal to 3.982 ± 0.001 Å), at the same time $c = 4.11 \pm 0.003$ — (c of the irradiated sample without electrodes is equal to 4.085 ± 0.001 Å).

It should be noted that the decrease in lattice tetragonality was observed in $BaTiO_3$ (powders) where the fast neutron fluence 10^{18} n/cm^2 was followed by the anisotropic expansion of the lattice, but already at the integral flux of 10^{20} n/cm^2, the lattice became cubic [23]. It was also shown in [23] that irradiation of $PbTiO_3$ powders up to fluence $9 \cdot 10^{19}$ n/cm^2 results in a decrease in tetragonality, and

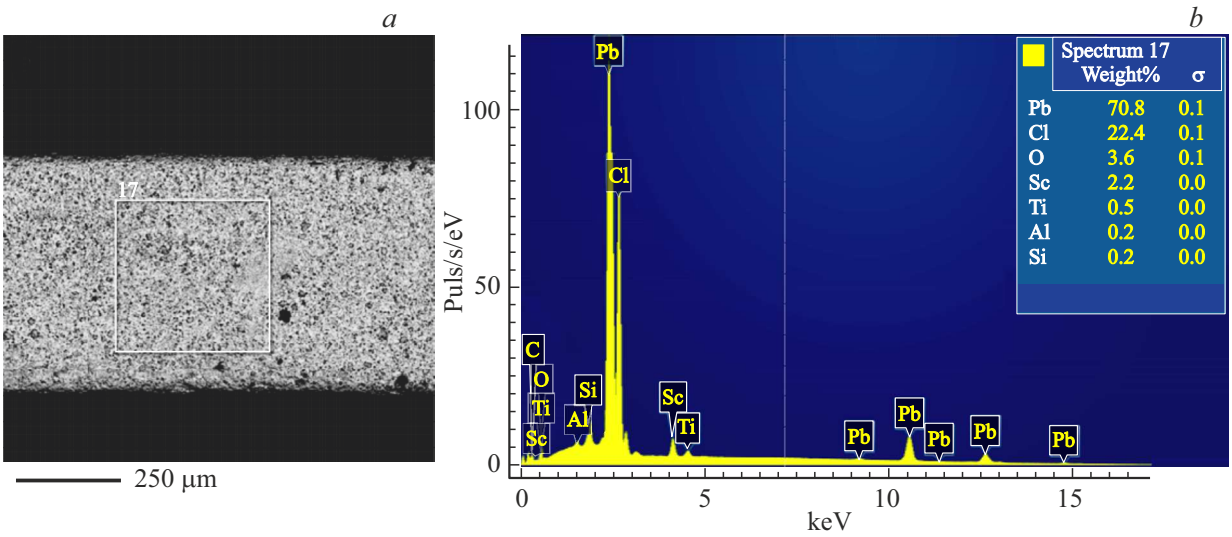

Figure 3. Electronic image of the radiation-exposed sample surface area after etching (a) and spectrum reflecting the elemental composition on the surface after etching (b).

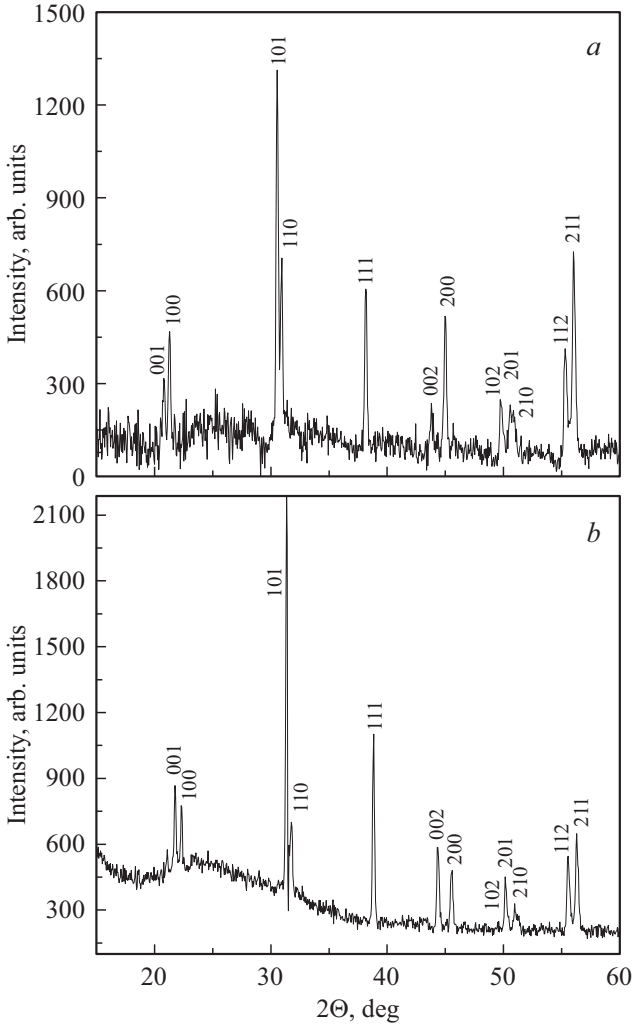

Figure 4. X-ray diffraction patterns of the near-electrode layer of the radiation-exposed $BiScO_3-PbTiO_3$ ceramics sample after removal of the gold electrode (a) and of the sample volume after irradiation (b).

the radiation-induced transition to the cubic phase occurs at fluence $\sim 10^{20}$ n/cm^2. The given examples of $BaTiO_3$ and $PbTiO_3$ refer to the effect of fast reactor neutrons ($E > 0.1$ MeV), when neutron irradiation can cause atomic displacements or a displacement cascade in the lattice depending on the energy transferred by neutrons to the crystal atoms. For BSPT piezoceramics, exposure with fluence $\sim 5 \cdot 10^{19}$ n/cm^2 ($E > 0.1$ MeV) resulted only in an increase in tetragonality by 0.47% within the sample [15]. For the Au electrode-BSPT ceramics interface, the observed experimental result likely corresponds to the initial stage of radiation-induced lattice degradation, which occurs when the concentration of defects in the near-electrode layer increases compared with the volume. Such defects can be, for example, Frenkel defects or impurity defects [24] that can be formed by Au atoms penetrating into the near-electrode layer due to the process of radiation-induced diffusion. With fluence increase, this process can end in the transformation of the tetragonal structure of the near-electrode layer into the cubic structure followed by amorphization detected during irradiation of $BaTiO_3$ and $PbTiO_3$ [23,24].

4. Conclusion

The effect of intense (fluence $\sim 5 \cdot 10^{19}$ n/cm^2, $E > 0.1$ MeV) fast neutron and gamma-quanta fluxes on the gold electrode — $BiScO_3-PbTiO_3$piezoceramics interface and directly on the gold electrode was investigated. Elemental composition of the electrode and interface, as well as the interface crystal structure after irradiation were measured. The results indicate that there is radiation-induced diffusion of gold into ceramics, as well as of Pb, and to a lesser extent Bi, Sc, Ti, to the surface. The process may be characterized as „radiation-induced mixing“. The

effect of radiation on the interface crystal structure results in radiation-induced expansion of the crystal lattice with an anisotropic increase in parameters and a decrease in tetragonality to $c/a = 1.024$. This may indicate the initial structural degradation stage. All results suggest a significant effect of radiation on the electrode-ceramics interface, which can affect the electrophysical properties of ceramics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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