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Effect of neutron irradiation on the elemental composition and structure of $BiScO_3$–$PbTiO_3$ ceramics

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Ceramics $0.64BiScO_3$–$0.36PbTiO_3$ were synthesized and its radiation resistance was studied. The experiments on irradiation of ceramic samples with fast neutrons and gamma rays in a pool-type reactor were carried out to analyze possible radiation damage. The irradiation conditions in terms of the accumulated fluence of neutrons and gamma quanta ($\sim 5 \cdot 10^{19}$ n/cm^2(γ/cm^2) at $E > 0.1$ MeV), as well as the energy spectrum, are close to those expected at the location of piezoelectric motors using this ceramics which are being developed within the ITER project. The elemental composition and crystal structure of the ceramics were determined before and after irradiation. The experimental results demonstrate the stability of the composition to high doses of radiation.

Keywords: piezoelectric ceramics, neutron irradiation, elemental composition, crystal structure.

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1. Introduction

Piezoelectric ceramics are widely used as an active material in piezoelectric transducers for ultrasonic non-destructive testing, sensors of various physical quantities, as well as in micromechanical systems for precision control and monitoring of nano-, micro- and macro-displacements. The latter include piezoelectric drives (actuators) and piezoelectric motors [1–4]. Of particular interest are high-temperature compositions that can significantly expand the range of operating temperatures above 150°C, typical for the widely used lead zirconate titanate (PZT) piezoceramics [5]. Modified solid solutions based on PZT have a Curie temperature in the range of 300−350°C, which results in a good temperature stability of piezoelectric properties and expands the operating temperature range to approximately 175°C taking into account the depolarization process [5–7]. Solid solutions of $BiScO_3-PbTiO_3$ and compounds based on this system are characterized by higher temperatures of the ferroelectric phase transition ($T_c = 450-500$°C), rather high piezoelectric coefficients, and, accordingly, are considered as promising high-temperature piezoelectric materials [8–13]. Such materials, in particular, turned out to be in demand for implementing power elements of piezoelectric motors [14] being developed within the framework of the International Thermonuclear Experimental Reactor (ITER) project. The objective of the ITER project is to demonstrate the possibility of commercial use of the nuclear fusion reaction (obtaining a positive yield with efficiency > 10%) and solving physical and technological problems that may arise along this path.

The use of piezomotors in the project is expected to control dozens of „shutters“ [15] used to protect the mirrors of the optical diagnostic system from erosion and deposition of materials during the combustion of thermonuclear plasma at high thermal and neutron/gamma-quantum fluxes. In the process of irradiation with gamma quanta, which accompanies neutron irradiation, the primary cause of radiation degradation of piezoceramics is depolarization, because gamma rays interact with the electronic subsystem, causing ionization, in contrast to neutrons, which interact directly with atomic nuclei [16]. The effect of irradiation on the electronic subsystem is beyond the scope of this study.

In the process of neutron irradiation, materials can significantly change their properties due to amorphization, changes in mechanical properties, and also due to transmutation of their elemental composition. It is clear that there is a significant challenge in selecting or developing piezoceramics that can withstand significant neutron damage and maintain the required performance characteristics, such as electromechanical properties and a wide range of operating temperatures. The estimated fluence of neutrons and gamma quanta during operation of the piezoelectric motor in the ITER reactor is $\gtrsim 10^{19}$ n/cm^2 ($E > 0.1$ MeV) [17], and the temperature regime during operation includes periodic heating to 250−300°C for 24 h. It should be noted that a significant change in the properties of piezoceramic materials of the PZT system is observed

even at integral fluence of fast neutrons above 10^{17} n/cm^2 ($E > 0.1$ MeV) [14,18].

For the synthesis and research purposes, the $0.64BiScO_3-0.36PbTiO_3$ solid solution was chosen, located near the morphotropic phase boundary (MPB), characterized by a high transition temperature to the paraelectric phase of $T_c = 450°C$ [19]. It should be noted that the depolarization of ceramic samples of this system with a composition near the MPB begins at temperatures above 300°C [20], which exceeds the upper limit of the temperature regime during operation in the ITER reactor. The assumption about the possible radiation resistance of this compound arose, among other things, due to the high content of lead titanate, which, according to the literature data [21,22], has exhibited resistance of the tetragonal structure to irradiation under radiation exposure to high-energy neutrons and gamma-rays quanta with a fluence of up to $\sim 10^{20}$ n/cm^2 ($E > 0.1$ MeV). The stability of the elemental composition and crystal structure of the material is a necessary condition for the use of ceramics when exposed to the radiation, and is also of interest from the point of view of the fundamental problem of the effect of radiation on the substance.

2. Experiment

Ceramic samples of the $0.64BiScO_3-0.36PbTiO_3$ solid solution were prepared using conventional ceramic techniques. The Bi_2O_3, Sc_2O_3, TiO_2, and PbO oxides were used as starting reagents. The samples were preliminary calcined in platinum crucibles at a temperature of 850°C for 4 h. The resulting powders were pressed into disks with a diameter of 10 mm and a thickness of 1.5–2 mm at a pressure of 8 MPa. The samples were finally at sintered a temperature of 1100°C for 2 h. During the preparation process, special measures were taken to prevent loss of lead and maintain the stoichiometry of the composition. To do this, during sintering, the samples in a platinum cup were covered with a second platinum cup of smaller diameter, and the space between the cups was filled with $PbZrO_3$ powder. Losses of PbO by weight were less than 1%. For X-ray diffraction (XRD) studies of the fabricated samples, a DRON-3 X-ray diffractometer with CuK_α radiation, $\lambda = 1.54178$ Å, Ni-filter, 38 kV, 18 mA was used. Scanning was carried out in the 2θ angle range from 10 to 60° with a step of 0.1°. When measuring lattice constants, germanium was used as a reference. X-ray diffraction measurements showed that the virgin samples were single-phase and had a perovskite structure. The density of the samples was 93–96% of the theoretical X-ray density. The analysis of the elemental composition of ceramics was carried out using a Tescan Mira scanning electron microscope with a system to determine the elemental composition. Measurements were carried out on both virgin samples and samples after exposure to radiation. The ceramics were radiation-tested in the VVR-M reactor of the „Kurchatov Institute“ National Research Center — PNPI. A channel in the reactor core was chosen for the irradiation. The container with the samples consisted of sealed ampoules nested inside each other. The space between the ampoules was filled with boron carbide to minimize the induced radiation activity and to form a neutron spectrum close to the spectrum expected in the ITER reactor. The total irradiation fluence was $5 \cdot 10^{19}$ n/cm^2 ($E > 0.1$ MeV). The analysis showed that, taking into account the heat release in the samples, containers, and the boron carbide screen, the temperature of the samples during irradiation was about 200°C. After exposure to neutrons, the samples „cooled“ for 8–10 years to a level allowing for measurements. Ceramic samples both without electrodes and with electrodes were studied, taking into account the need for electrodes when using piezoceramics. Gold sputtered onto the surface of the sample was used as the material for the electrodes.

3. Results and discussion

The elemental composition of samples of the $0.36BiScO_3-0.64PbTiO_3$ solid solution was measured before and after irradiation. For a virgin sample, the composition was determined at the at the front edge of the sample, as in the bulk (at a distance of 315 μm from the surface, section 9, section area is $S = 87444\,\mu$m^2, Figure 1, *a*), and in the near-surface layer (55 μm from the surface, section 10, section area is $S = 55555\,\mu$m^2, Figure 1, *a*) with a sample thickness of 685 μm. Relatively large areas S determine the reliability of composition measurements. For the irradiated sample, measurements were also carried out at the front edge of the sample, at a depth of 341 μm (section 5, $S = 113229\,\mu$m^2, Figure 2, *a*) and at a distance of 68 μm from the surface (section 6, $S = 24391\,\mu$m^2, Figure 2, *a*) with a sample thickness of 705 μm.

A comparison of the elemental composition of the bulk and surface layer of ceramics before and after irradiation is given in Tables 1 and 2.

It can be seen from the figures and tables that there is a weak dependence of the change in the weight composition

Table 1. Weight content of chemical elements in the bulk $BiScO_3-PbTiO_3$ ceramics before and after neutron irradiation

Element	Pb	Bi	Ti	Sc	O
Weight, %	Before irradiation				
	42.4	23.6	9.0	5.2	19.5
	After irradiation				
	42.1	23.2	8.9	5.4	20
	Change in weight content, %				
	−0.7	−1.7	−1.1	−3.8	+2.6

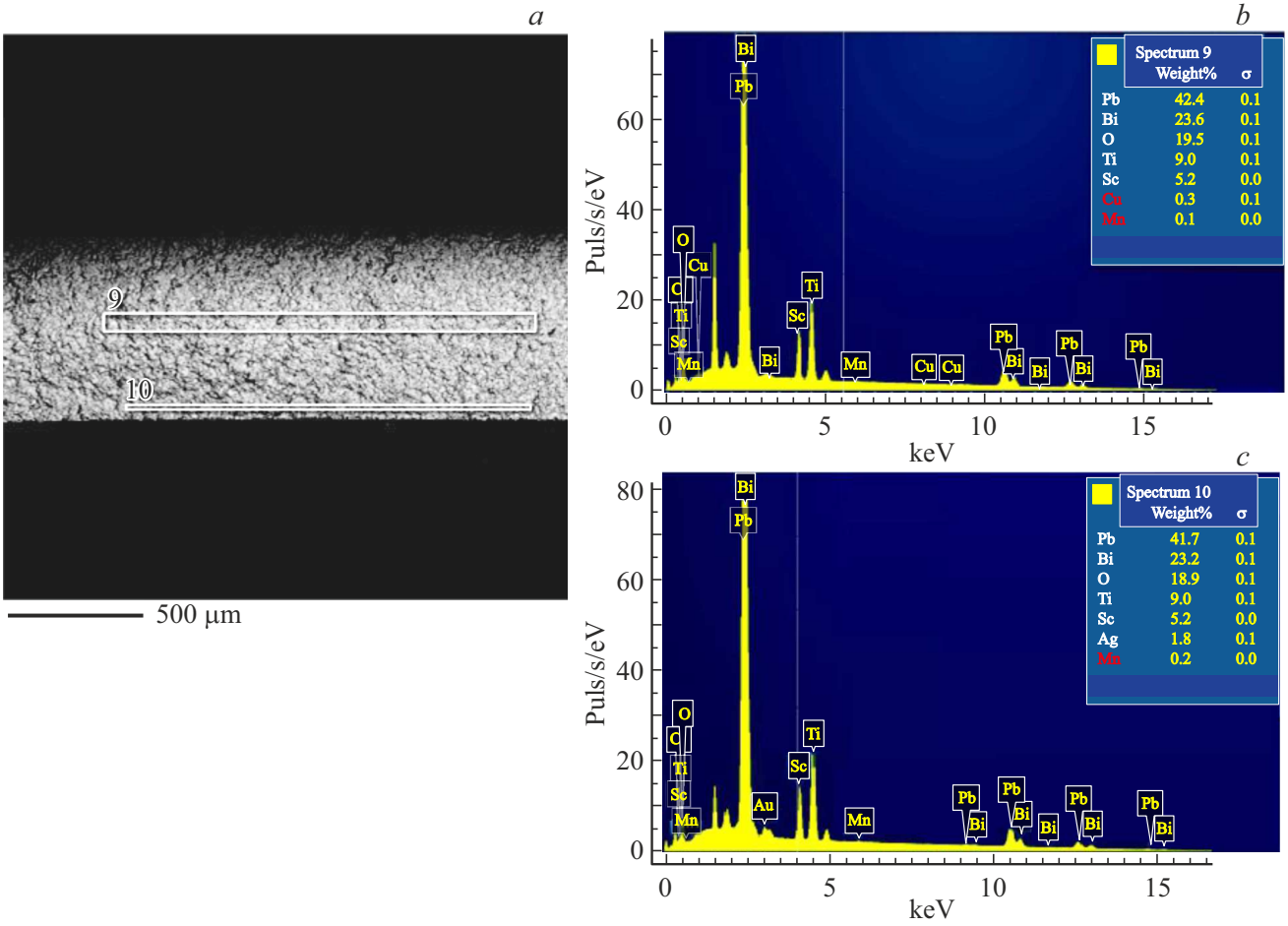

Figure 1. Electronic image of sections (9) and (10) of a virgin sample (*a*) and spectra reflecting the elemental composition in these sections, (*b*) and (*c*), respectively.

for the virgin and irradiated samples both in the bulk of the sample and in the near-surface region. Whereas some losses in weight content are observed for the Pb and Bi elements in the bulk, in the near-surface layer there is a slight increase in the weight content of Pb after irradiation. Perhaps lead and bismuth oxides come out from the bulk to the surface, similar to the processes of evaporation of these oxides during the synthesis of ceramics [23], which is also manifested in an increase in the weight content of the oxygen element on the surface after irradiation. Noteworthy is the increase in the weight content of Sc in the bulk against the background of a decrease in the Ti content. When a medium is irradiated with fast neutrons, the following reaction is possible [24]:

$$\mathrm{Ti}_{22}^{46} + n_0^1 \rightarrow \mathrm{Sc}_{21}^{46} + p_1^1 + \gamma,$$

where n_0^1 is neutron, p_1^1 is proton, γ is gamma radiation.

The fundamental possibility of such a reaction qualitatively explains the increase in the Sc content in the bulk after irradiation. At the same time, the problem of changes in the content of scandium and titanium after irradiation requires additional experimental study.

As already noted, it is the flux of fast neutrons with an energy of $E > 0.1$ MeV that determines, under ITER conditions, the degree of radiation damage occurring due to displacements caused by direct elastic collisions with nuclei, which result in the transfer of kinetic energy to these nuclei [1,14]. The nuclide composition of ceramics before and after irradiation in the sample placement area [25]

Table 2. Weight content of chemical elements in the near-surface layer of $BiScO_3-PbTiO_3$ ceramics before and after neutron irradiation

Element	Pb	Bi	Ti	Sc	O
Weight, %	Before irradiation				
	41.7	23.2	9.0	5.9	18.9
	After irradiation				
	42.1	23.2	8.9	5.4	20
	Change in weight content, %				
	+0.9	0	−1.1	−8.5	+5.8

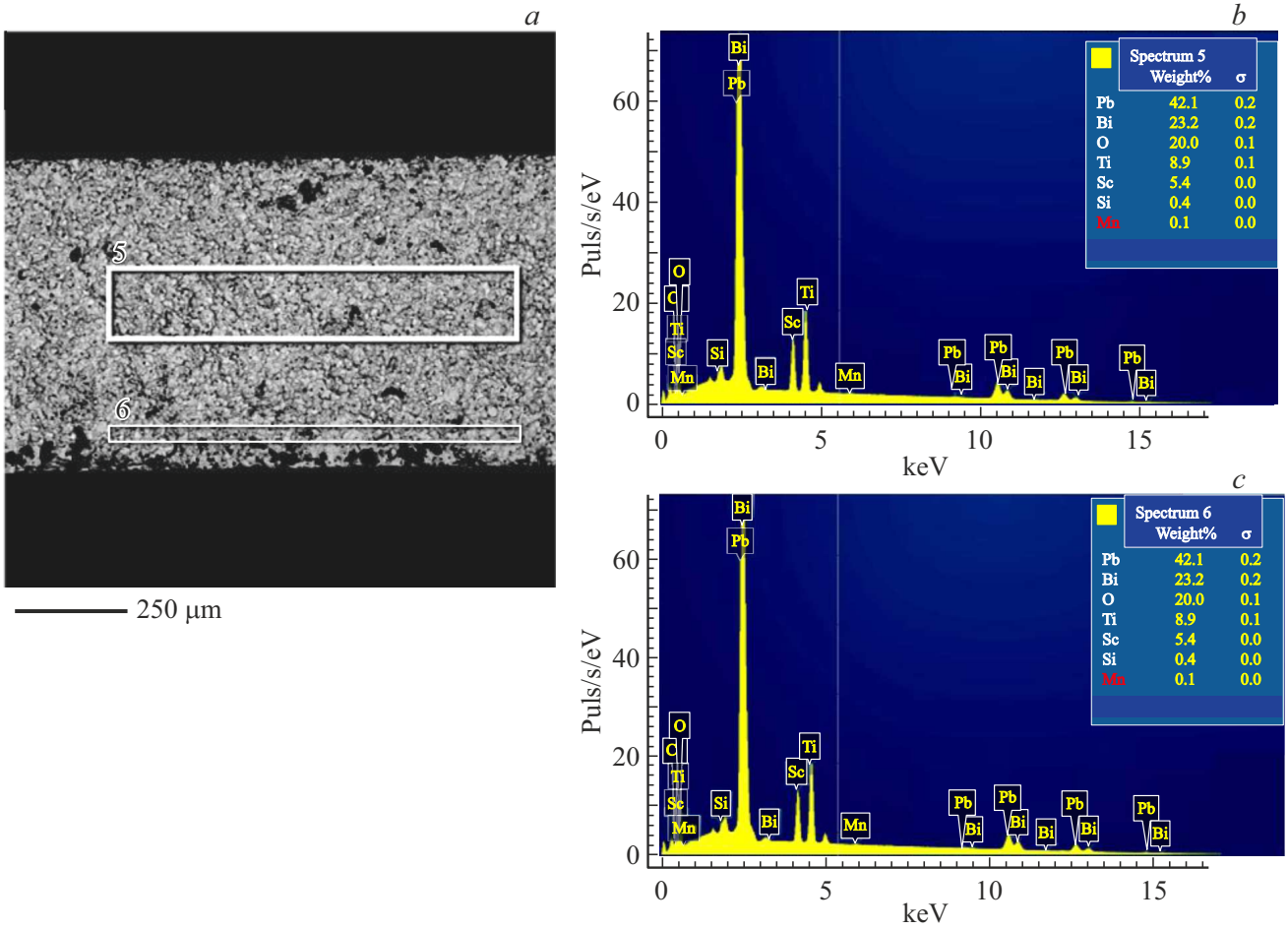

Figure 2. Electronic image of sections (5) and (6) of an irradiated sample (*a*) and spectra reflecting the elemental composition in these sections, (*b*) and (*c*), respectively.

was calculated using the FISPACT-II system [26] and a library of constants [27]. According to the results obtained, the expected neutron fluxes do not lead to a change in the percentage content of elements (the total nuclide composition of each element) of a given solid solution. The result of comparing the elemental composition of ceramics before and after irradiation obtained experimentally is qualitatively consistent with the calculation conclusion about the negligible effect of neutron fluence $\sim 10^{19}$ n/cm^2 on the elemental composition.

The structure of virgin and irradiated samples of the $0.36BiScO_3-0.64PbTiO_3$ solid solution located on the MPB is identified as a tetragonal structure ($P4mm$), similar to the structure of $PbTiO_3$ (Figure 3). In the irradiated sample, similar reflections (001) and (100), (002) and (200) are more pronounced compared to the virgin one, and a splitting of the (101) reflection into two reflections (101) and (110) for the irradiated sample.

The listed reflections characterize the existence of a tetragonal phase and a relative increase in the degree of tetragonality in the irradiated sample. The lattice constants of the virgin and irradiated samples are $a = 3.987 \pm 0.002$ Å, $c = 4.071 \pm 0.002$ Å (before irradiation) and a=3.9820 ± 001 Å, c=4.085 ± 0.001 Å (after irradiation). Thus, a radiative change in the lattice occurs with an anisotropic change in the parameters, at which the parameter c increases. The degree of tetragonality of the crystal lattice, the ratio of parameters c/a, increases after irradiation from 1.021 to 1.026, i. e. by 0.47%, which indicates the preservation of the composition near the MPB with a little change detected in the percentage of elements. It is interesting that an increase in lattice tetragonality was also observed in the $PbTiO_3$ compound after irradiation to $4 \cdot 10^{19}$ n/cm^2 with subsequent destruction of the lattice at higher fluences of neutron radiation $> 10^{20}$ n/cm^2 [21,22].

The obtained result is extremely important for assessing the resistance of piezoceramics when exposed to neutron radiation, because the preservation of the crystal structure and the presence of the composition (even with little changes in the elemental composition) in the MPB region indicates the fundamental possibility of preserving the electrophysical properties inherent in the non-irradiated material.

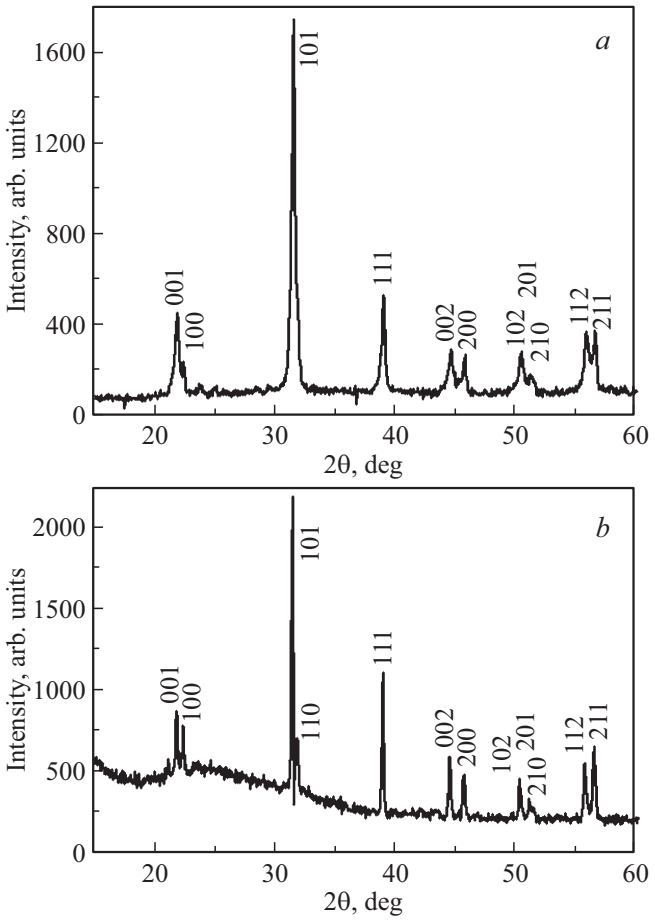

Figure 3. X-ray patterns of virgin *a*) and irradiated *b*) samples of $BiScO_3-PbTiO_3$ ceramics.

4. Conclusion

High-temperature ceramics with the composition of $0.36BiScO_3-0.64PbTiO_3$ have been synthesized. The effect of intense fluxes (fluence of $5 \cdot 10^{19}$ n/cm^2, $E > 0.1$ MeV) of fast neutrons on the elemental composition and crystal structure was investigated. The weight content of the elements in the composition was measured before and after irradiation. A slight change in the weight content of elements was detected both in the bulk and in the near-surface layer, at which the composition of the ceramics remains preserved near the morphotropic phase boundary. The crystal structure remains tetragonal, with the degree of tetragonality increasing by 0.47%. The results obtained indicate the radiation stability of the elemental composition and crystal structure of the $BiScO_3-PbTiO_3$ ceramics at a fluence of $5 \cdot 10^{19}$ n/cm^2, $E > 0.1$ MeV. This conclusion is an important indicator of the possibility to use such a ceramic material for the development of piezoelectric motors capable of functioning as part of optical diagnostic systems during the implementation of the ITER project.

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Conflict of interest

The authors declare that they have no conflict of interest.

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