

Effect of BiScO₃ Additive on the Structure and Electrical Properties of the Y₂O₃-ZrO₂-SrTiO₃ System

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Samples of ceramic systems Y₂O₃-ZrO₂-SrTiO₃ and Y₂O₃-ZrO₂-SrTiO₃-BiScO₃ were obtained. It was established that Y₂O₃-ZrO₂-SrTiO₃ is two-phase: the phase with the cubic structure $Pm\bar{3}m$, belonging to SrTiO₃, and the phase with the tetragonal structure ($P42/nmc$), belonging to Y_{0.05}Zr_{0.95}O₂. The introduction of the BiScO₃ component into the Y₂O₃-ZrO₂-SrTiO₃ system leads to the formation of three phases: the cubic phase with the space symmetry group $Fm\bar{3}m$, the cubic phase with $Pm\bar{3}m$ symmetry, and the tetragonal phase with $P4mm$ symmetry. The reflexes from the cubic phase of $Fm\bar{3}m$ belong to the cubic modification of zirconia. The cubic phase of $Pm\bar{3}m$ and the tetragonal phase of $P4mm$ belong to SrTiO₃-BiScO₃. Using scanning electron microscopy, it was shown that the addition of BiScO₃ additive to the Y₂O₃-ZrO₂-SrTiO₃ ceramic system leads to a significant decrease in the grain size and greater homogeneity of the material.

Based on the analysis of the results of studies of the specific electrical conductivity of the ceramic systems Y₂O₃-ZrO₂-SrTiO₃ and Y₂O₃-ZrO₂-SrTiO₃-BiScO₃, the introduction of the BiScO₃ additive into the ceramic system reduces the activation energy of the conductivity process from 1.5 eV to 0.82 eV.

Keywords: Ceramic system, X-ray phase composition, Microstructure, Conductivity.

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1. INTRODUCTION

One of the dynamically developing areas of hydrogen energy remains the development of solid oxide fuel cells (SOFC) due to their high efficiency of converting the chemical energy of hydrogen-containing fuel into electrical energy, silent operation, low toxicity [1]. Among the wide range of materials for the production of solid SOFC electrolytes in the high-temperature region, ceramic materials based on Y₂O₃-ZrO₂ are the most popular [2-3]. However, Y₂O₃-ZrO₂ achieves high conductivity at temperatures of 1000-1200 K [4]. To reduce the operating temperature, two approaches are applied: the use of thin-film coatings or the development of new systems operating at lower temperatures.

One of the first systems of thin-film electrolytes is the development of ZrO₂:Y₂O₃/SrTiO₃ heterostructures [5], ensuring the presence of voids in the coating structure along the ZrO₂:Y₂O₃/SrTiO₃ interfaces for the transport of oxygen ions associated with the disordering of the oxygen sublattice near the interface, which results to an increase in conductivity at lower temperatures.

An increase in the conductivity of bulk ceramic systems based on ZrO₂/SrTiO₃ is observed at temperatures above 650 K [6, 7].

The creation of solid solutions of multicomponent ceramic systems leads to the production of materials with desired properties, including those with high oxygen-ionic conductivity. The addition of BiScO₃ to the Y₂O₃-ZrO₂-SrTiO₃ system can result in a solid solution with high oxygen-ionic conductivity due to an increase in the structural disorder of the material and high ionic conductivity of Bi₂O₃ [8].

The purpose of this work was to determine the in-

fluence of BiScO₃ on the structure and electrical properties of the Y₂O₃-ZrO₂-SrTiO₃ system.

2. DESCRIPTION OF THE OBJECT AND METHODS OF STUDY

Obtaining samples of the Y₂O₃-ZrO₂-SrTiO₃ ceramic system with the composition 0.025 Y₂O₃, 0.475 ZrO₂, 0.5 SrTiO₃ consisted in the synthesis of SrTiO₃ from a mixture of strontium carbonate SrCO₃ and titanium dioxide TiO₂ annealed at 1623 K for 2 hours. The next step was to obtain a composition of 0.025 Y₂O₃, 0.475 ZrO₂, 0.5 SrTiO₃ from a mixture of powders of synthesized strontium titanate and Y_{0.05}Zr_{0.95}O₂, taken in a stoichiometric ratio. The mixture of powders was annealed at a temperature of 1623 K for 2 hours.

Samples of the Y₂O₃-ZrO₂-SrTiO₃-BiScO₃ ceramic system with the composition of 0.025 Y₂O₃, 0.475 ZrO₂, 0.3, 0.2 BiScO₃ were obtained according to the technology developed by us earlier in [9-10] as follows: previously synthesized SrTiO₃ powder and Bi₂O₃ and Sc₂O₃ oxides taken in stoichiometric ratio, were thermally treated at a temperature of 1523 K for 2 hours. The thus obtained powder and powder of zirconium dioxide stabilized with yttrium Y_{0.05}Zr_{0.95}O₂, taken in a stoichiometric ratio, were mixed in an agate mortar with the addition of ethyl alcohol for 4 hours. The received suspension was dried at 373 K for 1 hour.

Compaction of samples with a diameter of 10 mm and a thickness of 1 mm was performed by the method of biaxial pressing at a pressure of 70 MPa. Sintering of the samples was carried out at a temperature of 1543 K for 2 hours in an atmosphere of air. The phase composition of the material obtained was determined using a Rigaku Ultima IV X-ray diffractometer. The study of

the microstructure was carried out using a Quanta 200 3D raster ion-electron microscope, and the measurement of electrical conductivity σ and dielectric characteristics was performed on an Novocontrol Concept 43 impedance meter with alternating current.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

The diffractogram of the $Y_2O_3-ZrO_2-SrTiO_3$ ceramic system obtained at room temperature is shown in Fig. 1.

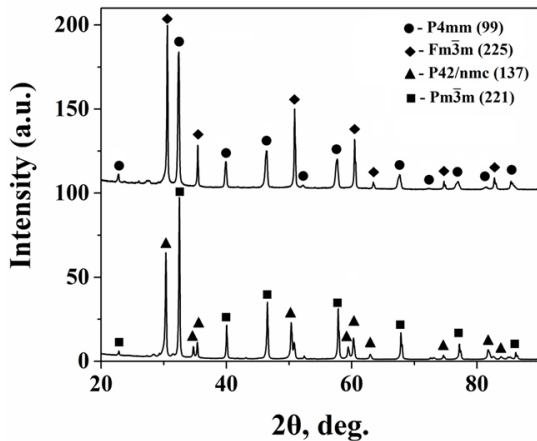


Fig. 1 – Diffractogram of the samples of the $Y_2O_3-ZrO_2-SrTiO_3$ ceramic system: \blacktriangle – tetragonal $P42/nmc$ phase; \blacklozenge – cubic $Fm\bar{3}m$ -phase; \bullet – tetragonal $P4mm$ -phase; \blacksquare – cubic $Pm\bar{3}m$ -phase

Based on the analysis of the diffractogram, it was found that the obtained $Y_2O_3-ZrO_2-SrTiO_3$ ceramic system is two-phase: a phase with a cubic structure (space symmetry group $Pm\bar{3}m$) and a phase with a tetragonal structure ($P42/nmc$). The reflexes from the cubic phase belong to $SrTiO_3$. The phase with tetragonal structure belongs to $Y_{0.05}Zr_{0.95}O_2$.

The introduction of the $BiScO_3$ component into the $Y_2O_3-ZrO_2-SrTiO_3$ system leads to the formation of three phases: the cubic phase with the space symmetry group $Fm\bar{3}m$, the cubic phase with the symmetry $Pm\bar{3}m$, and the tetragonal phase with the symmetry $P4mm$. Reflexes from the cubic phase of $Fm\bar{3}m$ are indexed as belonging to the cubic modification of zirconium dioxide. The cubic phase of $Pm\bar{3}m$ and the tetragonal phase of $P4mm$ belong to $SrTiO_3-BiScO_3$.

The SEM image of the sample surface of the ceramic system $Y_2O_3-ZrO_2-SrTiO_3$ (Fig. 2a, b) obtained in the phase contrast mode indicates that there are two types of grains in the sample structure: dark gray grains and light gray grains with dimensions of several micrometers. By the method of determining the elemental composition, it was established that lighter areas correspond to $Y_2O_3-ZrO_2$, dark areas – to $SrTiO_3$.

The results of measurements of the impedance of the $Y_2O_3-ZrO_2-SrTiO_3$ and $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic systems are presented in Fig. 4.

The impedance spectrum of the $Y_2O_3-ZrO_2-SrTiO_3$ ceramic system obtained at a temperature of 573 K (Fig. 5a) clearly shows two arcs due to contributions

from the grain volume, grain boundary, and growth at low frequencies associated with blocking electrodes.

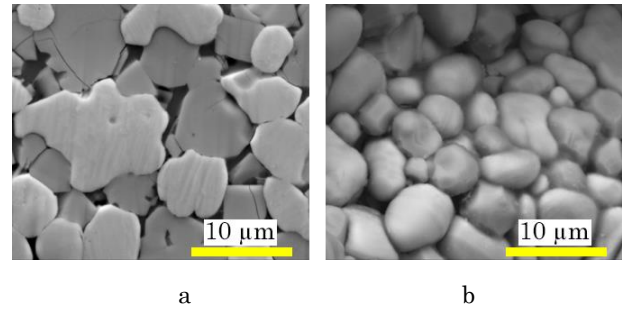


Fig. 2 – SEM-image of sample surface of the $Y_2O_3-ZrO_2-SrTiO_3$ ceramic system: a) thin section; b) chip

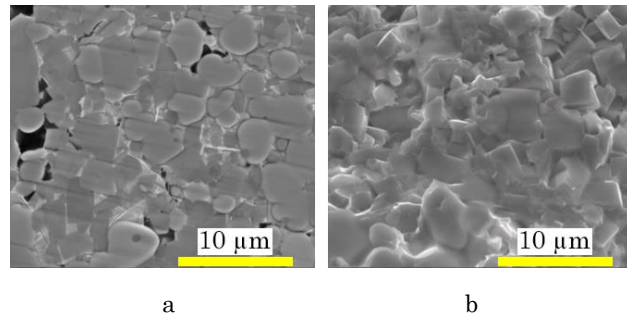


Fig. 3 – SEM-image of sample surface of the ceramic system $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$: a) thin section; b) chip

Fig. 3 a, b shows the SEM image of the sample surface of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system. In the presented images, grains of two types with sizes of ~ 1 micron are observed: grains of rounded shape and grains of rectangular shape. Using the definition of the elemental composition, it was established that grains of rounded shape correspond to the cubic $Fm\bar{3}m$ phase of zirconium dioxide. Grains having rectangular shape correspond to the compound of $SrTiO_3-BiScO_3$ solid solution.

The impedance spectrum of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system is a single circle at high frequencies and a blocking effect at low frequencies. The impedance spectrum of ceramic materials has two semi-circles indicating the contribution of the volume of grains and boundaries to the conductivity of the material. The presence of one circle in the impedance spectrum may be due to the high homogeneity of the obtained ceramic material [11], which is confirmed by images on the SEM image of a sample of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system.

The results of studies of the specific electrical conductivity of the ceramic systems $Y_2O_3-ZrO_2-SrTiO_3$ and $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ on an alternating current with a frequency of 1 kHz are presented in Fig. 5.

The temperature dependence of the electrical conductivity of ceramic systems $Y_2O_3-ZrO_2-SrTiO_3$ and $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ is determined according to the Arrhenius law:

$$\sigma = \sigma_0 \exp(-E_a / kT), \quad (1)$$

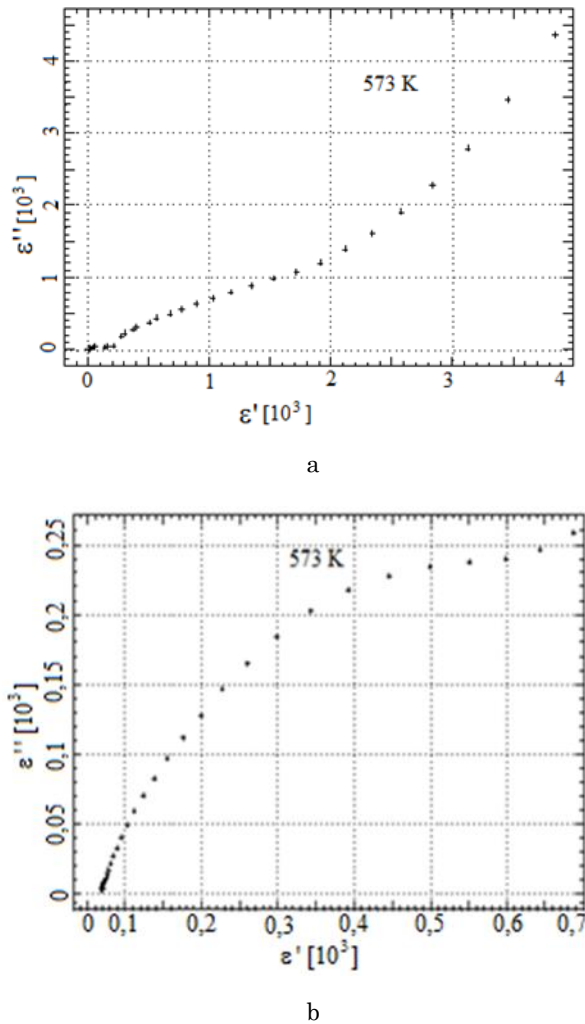


Fig. 4 – The impedance spectrum of ceramic systems in coordinates ε' (ε''): a) $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3$, b) $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$

where σ_0 is the pre-exponential factor; E_a is the activation energy of electrical conductivity; k is the Boltzmann constant equal to $1.38 \cdot 10^{-23}$ J/K.

The activation energy of the conduction process was 1.5 eV for the $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3$ system and 0.82 eV for the $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ system. Thus, we can conclude that the introduction of the BiScO₃ additive made it possible to reduce the activation energy approx-

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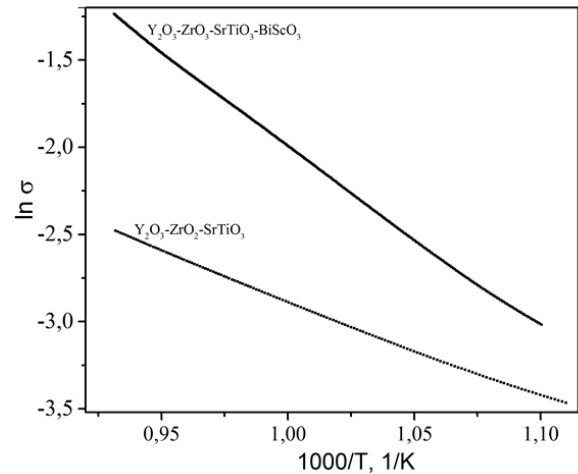


Fig. 5 – Dependence $\ln \sigma = f(1/T)$ of samples of ceramic systems $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3$ and $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$

imately by 2 times, and also to use the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ for the production of solid-state electrolytes.

4. CONCLUSIONS

1. It was found that $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3$ is two-phase: the phase with the $Pm\bar{3}m$ cubic structure belonging to SrTiO₃ and the tetragonal phase ($P42/nmc$) belonging to $\text{Y}_{0.05}\text{Zr}_{0.95}\text{O}_2$. The introduction of the BiScO₃ component into the $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3$ system leads to the formation of three phases: the cubic phase with the space symmetry group $Fm\bar{3}m$, the cubic phase with $Pm\bar{3}m$ symmetry, and the tetragonal phase with $P4mm$ symmetry. The reflexes from the cubic phase of $Fm\bar{3}m$ belong to the cubic modification of zirconia. The cubic phase of $Pm\bar{3}m$ and the tetragonal phase of $P4mm$ belong to SrTiO₃-BiScO₃.

2. Using scanning electron microscopy, it was shown that the addition of BiScO₃ additive to the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3$ leads to a significant decrease in the grain size and greater homogeneity of the material.

3. It has been established that the introduction of the BiScO₃ additive into the ceramic system leads to a decrease in the activation energy of the conduction process from 1.5 eV to 0.82 eV.

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Вплив домішки BiScO₃ на структуру та електричні властивості системи Y₂O₃-ZrO₂-SrTiO₃I.V. Суджанська¹, М.Н. Япринцев¹, Ю.С. Некрасова², В.М. Береснев³, А.Н. Васильев¹¹ *Белгородський державний національний дослідницький університет, вул. Перемоги, 85, 308015 Белгород, Росія*² *Белгородський державний технологічний університет ім. Шухова, вул. Костюкова, 46, 308012 Белгород, Росія*³ *Харківський національний університет ім. В.Н. Каразіна, пл. Свободи, 4, 61022 Харків, Україна*

В роботі отримано зразки керамічних систем Y₂O₃-ZrO₂-SrTiO₃ і Y₂O₃-ZrO₂-SrTiO₃-BiScO₃. Встановлено, що Y₂O₃-ZrO₂-SrTiO₃ є двофазною і складається із фази з кубічною структурою ($Pm\bar{3}m$), що належить до SrTiO₃, і фази з тетрагональною структурою ($P42/nmc$), що належить до Y_{0.05}Zr_{0.95}O₂. Введення компонента BiScO₃ у систему Y₂O₃-ZrO₂-SrTiO₃ призводить до утворення трьох фаз: кубічної фази з групою симетрії простору $Fm\bar{3}m$, кубічної фази з симетрією $Pm\bar{3}m$ та тетрагональної фази з симетрією $P4mm$. Рефлекси від кубічної фази $Fm\bar{3}m$ належать до кубічної модифікації діоксиду цирконію. Кубічна фаза $Pm\bar{3}m$ і тетрагональна фаза $P4mm$ належать до SrTiO₃-BiScO₃. За допомогою скануючої електронної мікроскопії було показано, що додавання добавки BiScO₃ до керамічної системи Y₂O₃-ZrO₂-SrTiO₃ призводить до значного зменшення розміру зерен і більшої однорідності матеріалу. Аналіз результатів досліджень питомої електропровідності керамічних систем Y₂O₃-ZrO₂-SrTiO₃ і Y₂O₃-ZrO₂-SrTiO₃-BiScO₃ свідчить, що введення добавки BiScO₃ в керамічну систему зменшує енергію активації процесу провідності від 1.5 eV до 0.82 eV.

Ключові слова: Керамічна система, Рентгенофазовий склад, Мікроструктура, Питома електропровідність.