

Electrical Conductivity and Dielectric Relaxation Processes of the Ceramic System Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$

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The ceramic system Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ was synthesized by the reaction method in the solid phase. The frequency and temperature dependences of the electrical conductivity of Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ ceramics are obtained. At a temperature above 500 K, the dielectric relaxation of the Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ ceramic system was detected, the activation energy of the relaxation process was 1.25 eV. It is established that the activation energy of the conduction process of the ceramic system Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ was 1.04 eV.

Keywords: Electrical Conductivity, Dielectric relaxation, Ceramic system.

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1. INTRODUCTION

At present, ceramic composites are used for the production of solid electrolytes, which meet the following criteria: high oxygen-ion conductivity, heat resistance, strength [1]. One of the basic materials corresponding to all criteria of solid electrolytes is zirconium. The use of zirconium oxide is limited by low electrical conductivity at room temperature (bandgap width > 5 eV) and the cubic phase is stable only at temperatures above 2570 °C [2-3]. The introduction of additives such as Y, Sc, Mg, Ca allows to stabilize the cubic structure of ZrO_2 at lower temperatures [4]. It is known that the ZrO_2 - Sc_2O_3 system possesses the highest conductivity from the above listed additives, but the use of such a system is limited by the degassing time, and conductivity characteristic of semiconductors is observed at temperatures of 800 °C-1000 °C [5].

The introduction of an impurity of Y_2O_3 leads to an increase in the degassing time in comparison with the addition of Sc_2O_3 , however, the Y_2O_3 - ZrO_2 system has a lower oxygen-ion conductivity than the ZrO_2 - Sc_2O_3 ceramic system [4]. It is known [7] that Bi_2O_3 possesses the greatest ionic conductivity, the lack of use of which is a low evaporation temperature of 700 °C, and this problem can be solved by a preliminary synthesis of the Bi_2O_3 - Sc_2O_3 system.

In addition, the film heterosystem Y_2O_3 - ZrO_2 / $SrTiO_3$ has a high conductivity at room temperature due to the creation of nonconducting $SrTiO_3$ layers [8].

The synthesis of the ceramic system Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ can allow to obtain a ceramic system characterized by high oxygen-ionic conductivity.

The search for conductive ionic materials requires a detailed study of the dynamics of ion motion in a solid. Information on ohmic losses, electrochemical kinetics, mass transfer processes, and the detection of charge transfer inhibition factors can be obtained by impedance spectroscopy [9].

The purpose of this work was to study the electrical conductivity and dielectric relaxation processes of the Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ ceramic system by impedance spectroscopy.

2. DESCRIPTION OF THE OBJECT AND METHODS OF THE STUDY

Preparation of samples of composition 0.5 (0.05 Y_2O_3 -0.95 ZrO_2)-0.5 (0.6 $SrTiO_3$ -0.4 $BiScO_3$) consisted in preliminary synthesis of $SrTiO_3$ by annealing a mixture of strontium carbonate $SrCO_3$ and titanium dioxide TiO_2 at 1623 K for 2 hours. Further, a composition of 0.6 $SrTiO_3$ -0.4 $BiScO_3$ was obtained from a mixture of powders of synthesized strontium titanate and Bi_2O_3 and Sc_2O_3 oxides taken in the stoichiometric ratio. The mixture of powders was annealed at a temperature of 1523 K for 2 hours.

The obtained composition 0.6 $SrTiO_3$ -0.4 $BiScO_3$ and zirconium dioxide stabilized with yttrium $Y_{0.05}Zr_{0.95}O_2$, taken in the stoichiometric ratio, were mixed in an agate mortar with the addition of ethyl alcohol for 4 hours, the resulting suspension was dried at 373 K for 1 hours. The compaction of samples with a diameter of 12 mm, a thickness of 1 mm, was carried out by biaxial pressing at a pressure of 70 MPa. Sintering of the samples was carried out at a temperature of 1543 K for 2 hours. All the processes of synthesis and sintering were carried out in an air atmosphere.

The phase composition of the obtained material was determined using a Rigaku Ultima IV X-ray diffractometer, σ and dielectric characteristics were measured on an Novocontrol Concept 43 impedance meter using alternating current.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

In Fig. 1 shows the diffractogram of the ceramic system Y_2O_3 - ZrO_2 - $SrTiO_3$ - $BiScO_3$ corresponding to the presence of three phases in the system: a cubic phase with a space symmetry group Fm3m corresponding to zirconium oxide, a cubic phase with Pm3m symmetry, and a tetragonal phase with P4mm symmetry corresponding to the $SrTiO_3$ - $BiScO_3$ compound.

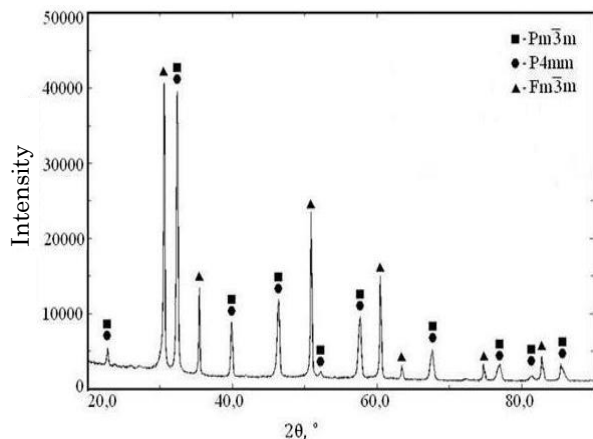


Fig. 1 – Diffractogram of the ceramic system $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$; \blacktriangle – cubic $Fm\bar{3}m$ -phase; \blacksquare – cubic $Pm\bar{3}m$ -phase; \bullet – tetragona $P4mm$ -phase

In Fig. 2 the impedance spectrum constructed in the complex plane ($\varepsilon'' = f(\varepsilon')$), characteristic for solid solutions, is presented.

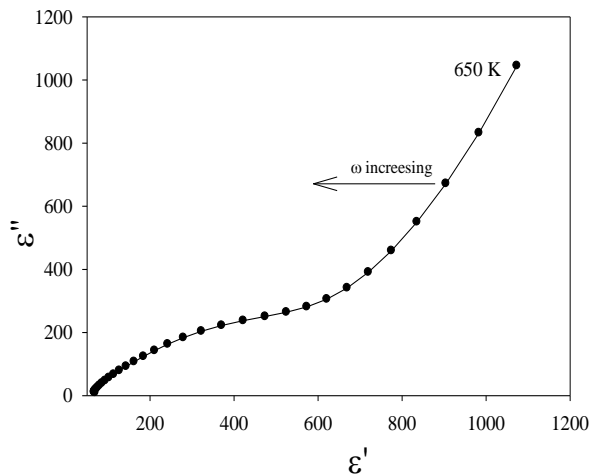


Fig. 2 – Impedance spectrum of the ceramic system $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$, obtained at a temperature of 650 K

Two relaxation processes are observed on the impedance spectrum: a high-frequency arc (cyclic frequency ω), which is associated with the transport of oxygen inside the grain volume and the growth observed at low frequencies caused by the motion of oxygen ions in the concentration gradient near the solid electrolyte-electrode boundary.

It is known that the impedance spectrum of polycrystalline materials in the complex plane has two circles, indicating a contribution to the overall conductivity of the material of the grain size and their boundaries. In our case, only one circle is observed, which may be due to the high homogeneity of the samples [9].

Figure 3 shows the conductivity spectrum of $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramics in alternating current as a function of frequency at different temperatures.

Analysis of the spectrum of the frequency dependence of the conductivity of the ceramic sample $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ shows a strong dependence on the measured temperature. In the low-temperature region, a monotonous increase in the electrical conductivity is observed

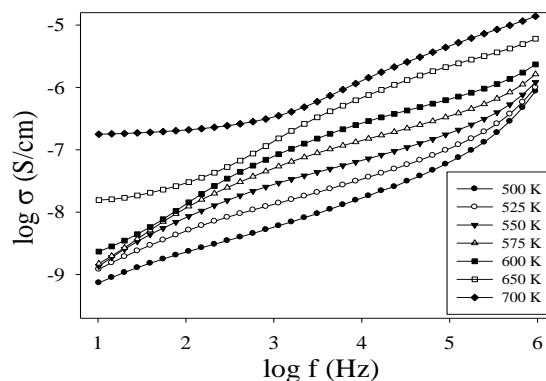


Fig. 3 – Spectrum of the frequency dependence of the electrical conductivity of the ceramic system $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ on temperature

at low frequencies, depending on the frequency, at high frequencies, the exponential dependence of the electrical conductivity on the frequency of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system.

At temperatures above 500 K, a protrusion associated with dielectric relaxation is observed. As the temperature rises, the protrusion moves into the region of high frequencies. The presence of inhomogeneities in the frequency dependence of the specific electrical conductivity of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system observed on the spectrum is confirmed by the results of studies of the dielectric constant and the tangent of the dielectric loss angle on frequency (Fig. 4-5).

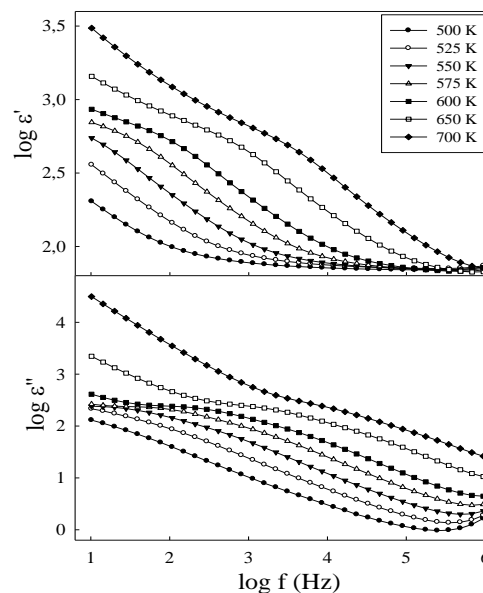


Fig. 4 – Logarithmic dependence of the imaginary (ε'') and real (ε') parts of the dielectric constant of the ceramic system $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ on frequency

The frequency dependencies of the dielectric loss tangent ($\tan \delta$) of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system at different temperatures are shown in Fig. 5.

Analysis of the frequency dependence of the dielectric loss tangent ($\tan \delta$) of the $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ ceramic system at different temperatures demonstrates the presence of a maximum whose temperature depends on the

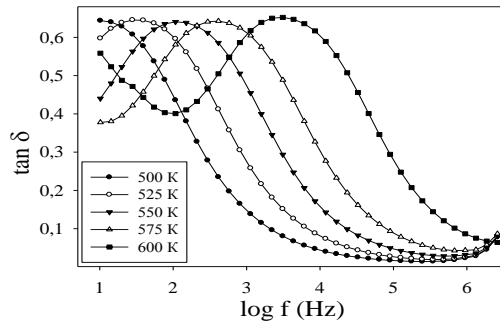


Fig. 5 – Dependence of the dielectric loss tangent ($\tan \delta$) of the $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ ceramic system at different temperatures on frequency

measured frequency—as the frequency decreases, the maximum shifts toward low temperatures. The revealed characteristics of dielectric permittivity and tangent of the dielectric loss angle are inherent in the process of dielectric relaxation.

The process of dielectric relaxation (Debye-type relaxation) is characterized by a relaxation time (τ) and an activation energy. The relaxation time is given by:

$$\tau = \frac{1}{2\pi f}, \quad (1)$$

where f is the measured frequency. According to the Arrhenius law

$$\tau = \tau_0 \exp\left(-\frac{U}{kT}\right), \quad (2)$$

where U is the activation energy of the relaxation process; k — the Boltzmann constant, equal to 1.38×10^{-23} J/K; τ_0 – pre-exponential factor.

The activation energy of the relaxation process, determined from the slope of the linear dependence (Fig. 6), was 1.25 eV.

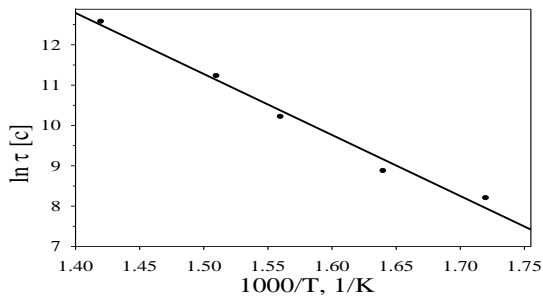


Fig. 6 – Logarithmic dependence of the relaxation time of the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ on the temperature

Figure 7 shows the temperature dependence of the electrical conductivity of the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ in the coordinates $\ln \sigma(1/T)$, according to the Arrhenius law:

$$\sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right), \quad (3)$$

Where σ_0 is the pre-exponential factor; E the activation energy of electrical conductivity;

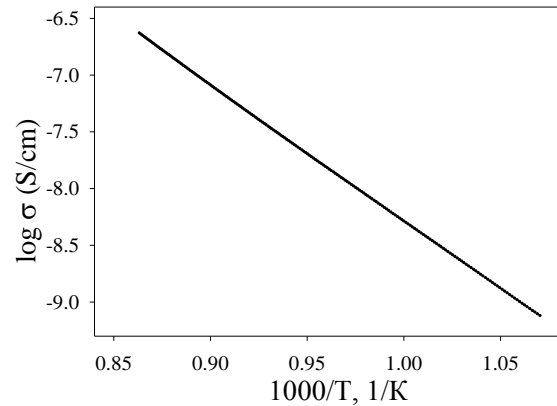


Fig. 7 – Temperature dependence of electrical conductivity of the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$

The activation energy of the conduction process of the $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ ceramic system, calculated from the slope of the linear dependence (Fig. 7), was 1.04 eV, which makes it possible to use this system for the production of solid electrolytes.

4. CONCLUSION

Samples of the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ are obtained. X-ray spectral analysis revealed the presence of three phases in the system: a cubic phase with a space symmetry group $Fm\bar{3}m$ corresponding to zirconium oxide, a cubic phase with $Pm\bar{3}m$ symmetry, and a tetragonal phase with $P4mm$ symmetry corresponding to the $\text{SrTiO}_3\text{-BiScO}_3$ compound.

The frequency dependence of the electrical conductivity of $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ ceramics at different temperatures is obtained. It is shown that in the low-temperature region at low frequencies monotonous growth of the specific electrical conductivity is observed as a function of frequency, at high frequencies – the exponential dependence of the electrical conductivity on the frequency of the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$. At a temperature above 500 K, the dielectric relaxation of the $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ ceramic system was detected, the activation energy of the relaxation process was 1.25 eV. The activation energy of the conduction process of the ceramic system $\text{Y}_2\text{O}_3\text{-ZrO}_2\text{-SrTiO}_3\text{-BiScO}_3$ was 1.04 eV.

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Электропроводимость и процессы диэлектрической релаксации керамической системы $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$

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Методом реакции в твердой фазе синтезирована керамическая система $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$. Получены частотная и температурная зависимости электропроводности керамики $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$. При температуре выше 500 К обнаружена диэлектрическая релаксация керамической системы $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$, энергия активации процесса релаксации составила 1,25 эВ. Установлено, что энергия активации процесса проводимости керамической системы $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ составила 1,04 эВ.

Ключевые слова: Электропроводимость, Диэлектрическая релаксация, Керамическая система.

Електропровідність та процеси діелектричної релаксації керамічної системи $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$

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Методом реакції в твердій фазі синтезована керамічна система $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$. Отримано частотну та температурну залежності електропровідності кераміки $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$. При температурі вище 500 К виявлено діелектрична релаксація керамічної системи $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$, енергія активації процесу релаксації склала 1,25 еВ. Встановлено, що енергія активації процесу провідності керамічної системи $Y_2O_3-ZrO_2-SrTiO_3-BiScO_3$ склала 1,04 еВ.

Ключові слова: Електропровідність, Діелектрична релаксація, Керамічна система

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