

Radiation modification of $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$

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The effect of irradiation with electrons and ions of inert gases (Ne, Ar, Kr) and oxygen of various energies on the structure, surface state and gaseous components in $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$ has been studied. It was shown that electron irradiation of $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$ results in smoothing-out of the irradiated surface relief, while electron irradiation of BaCeO_3 led to formation of a fine pyramidal (needle-shaped) structure on the irradiated surface. It was noted that in case of $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$ irradiation with high-energy inert gas ions, solid-phase transformations occurred on the surface of $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$. The conclusion was made about the mechanism of the influence of irradiation with high and low energy heavy ions of inert gases on the state of the gaseous components in $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$, based on the features of defects formation under irradiation with the ions of different energies.

Keywords: Proton conductivity, barium cerate, radiation modification, inert gas ions

INTRODUCTION

Currently, active research is being conducted in the area of hydrogen energy. Fuel cells based on solid proton-conducting electrolytes with the ABO_3 perovskite structure, capable of directly converting the chemical energy of hydrogen into electrical energy, are considered as one of the most promising alternative sources of electricity [1, 2].

In the initial state, the perovskite of the ABO_3 type is a dielectric and to give it the properties of proton conductivity, the so-called acceptor doping is traditionally performed, that is, the tetravalent cation at position B is partially replaced by the trivalent rare earth element Re, resulting in formation of oxygen vacancies $\text{V}^{\bullet\bullet}$ with an effective charge of +2 in the lattice. The newly formed compound can be written as follows: $\text{AB}_{1-x}\text{Re}_x\text{O}_{3-\delta}$, where x is the concentration of the trivalent cation or the degree of doping, and $\delta = x/2$ is the concentration of oxygen vacancies. When doped perovskite is exposed in a humid atmosphere, dissociative dissolution of water vapor takes place in the barium cerate lattice in accordance with reaction (1).



The diffusion of protons to the oxygen ions provides the proton conductivity of the oxide.

A deterrent to the widespread use of fuel cells based on proton conductors is currently the high cost of electricity produced due to the high cost of fuel and fuel cell materials, their low stability and efficiency. Therefore, an active search for materials of highly efficient and stable electrolytes is currently in progress. The main focus here is the synthesis of new compounds with the property of proton (ionic) conductivity.

In recent years, there have been proposed to increase the efficiency of ionic conductors through their radiation modification [3-5].

Earlier we have reported some results on influence of irradiation [7] and cation dopant type on structure and properties of barium cerates [9, 10].

In this paper the new results on effect of irradiation with electrons, as well as oxygen, neon, argon and krypton ions of various energies on the structure and properties of $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$ are presented.

EXPERIMENTAL TECHNIQUE

Samples of ceramic $\text{BaCe}_{0.85}\text{Nd}_{0.15}\text{O}_{3-\delta}$ in the form of plates of 10x5x1 mm size were preliminarily annealed in air at the temperature of 650°C for 7 hours.

Some of the samples were irradiated with heavy ions at the accelerator DC-60 of the Institute of Nuclear Physics of the Republic of Kazakhstan, Astana. Tab.1 shows the irradiation characteristics, as well as the ion ranges and

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damages, calculated using the SRIM - 2013 software [6].

Table 1. Results of calculations of the ion ranges and the concentration of vacancies

High energy			
Ion type	Ion energy, [MeV]	Ion range, [μm]	Vacancy/ion
Ne ⁺	35	12.7	2700
Ar ⁺	70	13.2	8100
Kr ⁺	147	15.3	31000
O ⁺	28	13.3	1740
Low energy			
Ion type	Ion energy, [keV]	Ion range, [μm]	Vacancy/ion
Ne ⁺	40	0.065	320
Ar ⁺	100	0.080	800
Kr ⁺	260	0.108	2500
O ⁺	40	0.080	243

Along with this, some of the samples were irradiated with 1.3 MeV electrons at the accelerator ELV-4 of the INP RK up to doses of 1.0, 5.0, 10.0 and 14 MGy. The calculations showed that the maximum temperature of the irradiated face of the sample did not exceed 372 K.

In this work, the following methods were used: X-ray phase analysis using the diffractometer X'PertPRO, scanning electron microscopy with the microanalyzer JEOL JSM-6490, atomic force microscopy NT-MDT, thermal desorption spectroscopy using the RF mass spectrometer MX-7304, thermal analysis using the thermal analyzer EXSTAR -6000.

RESULTS AND DISCUSSION

X-ray phase analysis of the initial $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ samples annealed in air at 650°C showed that their structure corresponds to the perovskite structure of undoped $BaCeO_3$. Irradiation of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ with low-energy inert gas ions ($E=40 - 260$ keV) to doses of 10^{16} cm⁻² did not have a significant effect on the structure and parameters of the crystal lattice of the material. Also, no changes in the structure of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ were found after irradiation with low-energy oxygen ions and electrons. Irradiation of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ with the high-energy ions of inert gases led to partial amorphization of the irradiated surface of the material, while the non-irradiated side retained the original structure [7].

The study of the surface morphology of irradiated $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ by scanning electron microscopy showed that, depending on the type and energy of the ion, the surface of the

ceramics undergoes significant changes. Thus, the irradiation of the samples with low-energy neon ions led to formation of blisters on the surface of the complex oxide (Fig.1).

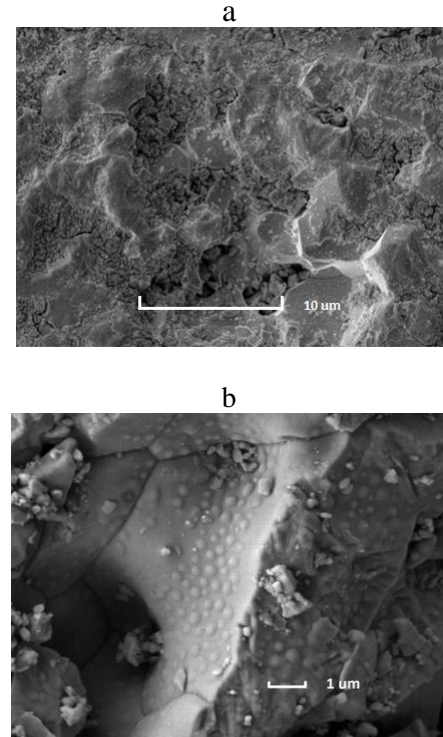
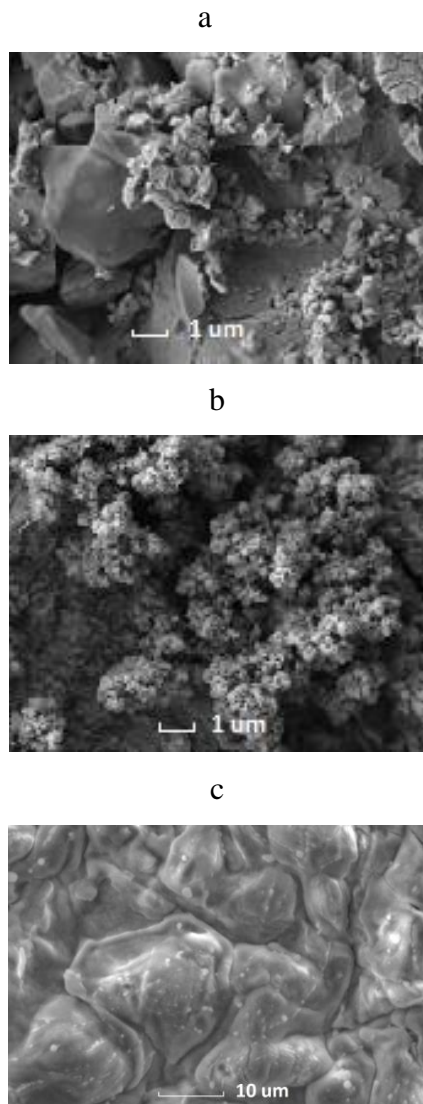


Fig.1. Electron microscopic images of the surface of barium cerate: a - unirradiated sample; b - irradiated with neon ions (40 keV, 10^{16} cm⁻²)

In case of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ irradiation with high-energy inert gases, there were changes apparently caused by the solid-state structural transformations on the surface, and in the series Ne, Ar, Kr the surface of the cerate resembled the growth stages of spherulites — nucleation, growth and formation of spherulitic crust (Fig.2).

It should be noted that after irradiation with high-energy oxygen ions, no similar changes in the structure and surface state of the barium cerate were observed, which indicates, apparently, the peculiarities of defect formation in case of cerate irradiation with the ions of inert gases and oxygen and, probably, due to the difference in their solubility. It is assumed that in the first case, the material is oversaturated with lattice defects by means of their stabilization by the ions of inert gas with formation of the “inert gas-vacancy” complexes. These complexes are highly stable due to low solubility of inert gases in the materials. This is confirmed by the absence of inert gases release from the samples in the experiments of thermal desorption up to 1000°C.



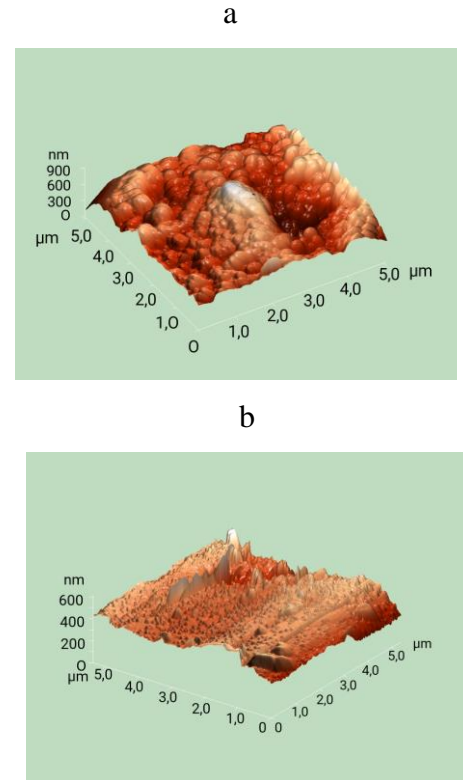
a – Ne, b – Ar, c – Kr ($D = 10^{16} \text{ cm}^{-2}$)

Fig.2. Electron microscopic images of the surface of barium cerate irradiated with high-energy inert gas ions

In case of irradiation of the composite oxide with the high-energy ions of oxygen at elevated temperatures, the equilibrium concentration of defects should be significantly lower. Indeed, the solubility of oxygen in cerate is significantly higher than that of inert gases, and when irradiated at elevated temperatures, oxygen can leave the material as a result of its diffusion to the surface and subsequent desorption. In this case, the stabilization of the defect structure does not occur, and a significant part of the defects, formed during irradiation, is annealed under irradiation.

It turned out that the surface relief of the samples, irradiated with electrons, depended substantially on their composition. Thus, electron irradiation of $BaCe_{0,85}Nd_{0,15}O_{3,8}$ led to a smoothing of the surface relief, while electron

irradiation of $BaCeO_3$ led to formation of a small pyramidal (needle) structure on the surface of the complex oxide (Fig.3). The height of the "pyramids" in this case did not exceed 50 nm.



a – unirradiated; b – electron irradiated.

Fig.3. AFM images of undoped barium cerate

Studies of the processes of thermal desorption of gases from barium cerate doped with Nd were carried out at the gas release unit described in details in [7]. Partial pressures of oxygen and water molecules were recorded with mass-spectrometer as a function of temperature during sample heating. This device allows to register up to 6 different gases simultaneously.

The conditions for the experiments on thermal desorption are as follows: the working vacuum in the chamber is no worse than 10^{-8} mm Hg, the heating rate of the samples is $42^\circ\text{C}/\text{min}$.

According to the thermal desorption spectroscopy data, irradiation with low-energy oxygen ions practically did not affect the state of the gaseous components, as evidenced by the fact that irradiation did not affect the thermal desorption of O_2 and H_2O .

At the same time, irradiation of $BaCe_{0,85}Nd_{0,15}O_{3,8}$ with both low-energy and high-energy ions of inert gases had a significant impact on the thermal desorption of oxygen and water molecules. First of all, we should note a

significant rise in the amount of desorbed oxygen from the $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ samples irradiated with the low-energy ions of inert gas (dose 10^{16} ions/cm²) compared with the non-irradiated samples. As it turned out, the amount of released oxygen from the samples, irradiated with different ions, was approximately the same (Fig.4).

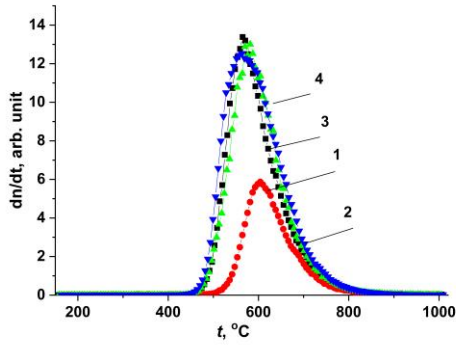


Fig.4. Oxygen release spectra from $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ after irradiation with low-energy ions: 1 – non-irradiated sample; 2 – irradiated with Ne ions; 3 – Ar; 4 – Kr ($D = 10^{16}$ cm⁻²)

Irradiation of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ with high-energy ions of inert gases, on the contrary, caused a decrease in the amount of desorbed oxygen compared to the unirradiated sample. It should be noted that the amount of desorbed oxygen decreased with a decrease in the mass of the implanted ion (Fig.5).

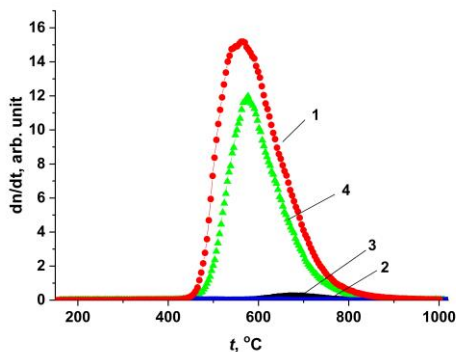


Fig.5. Oxygen release spectra from $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ after irradiation with high-energy ions: 1 – unirradiated sample, 2 – irradiated with Ne ions, 3 – Ar, 4 – Kr ($D=10^{16}$ cm⁻²)

Irradiation of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ samples with the low-energy ions of inert gases led to a significant decrease in the amount of desorbed water compared to the non-irradiated sample. As in the case of desorption of oxygen molecules, the amount of desorbed water from the samples, irradiated with different ions, was also approximately the same (Fig.6).

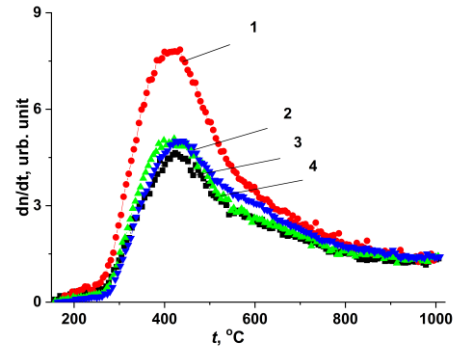


Fig.6. Water release spectra from $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ after irradiation with low-energy ions: 1 – non-irradiated sample; 2 – irradiated with Ne ions; 3 – Ar; 4 – Kr ($D = 10^{16}$ cm⁻²)

The opposite situation was observed when $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ was irradiated with the high-energy ions, i.e., the amount of water, desorbed from the irradiated sample, was more than that from the non-irradiated one. It should be noted that the maximum amount of water was released from the sample irradiated with the ions of neon (Fig.7). In this case, an insignificant low-temperature yield of water was observed in the spectra of thermal desorption of the irradiated samples.

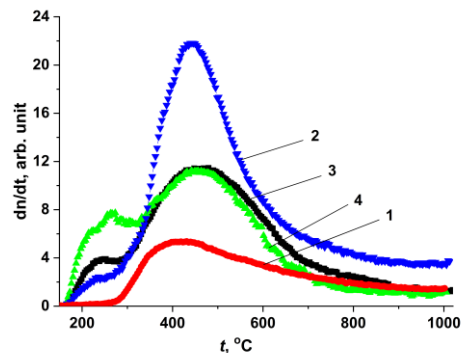
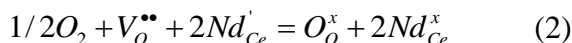


Fig.7. The spectra of water release from $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ after irradiation with high-energy ions: 1 – non-irradiated sample, 2 – irradiated with Ne ions, 3 – Ar, 4 – Kr ($D=10^{16}$ cm⁻²)

It should be noted that a feature of barium cerate, doped with neodymium, is the presence of superstoichiometric oxygen. This conclusion was first made in [8] when studying the oxygen nonstoichiometry of barium and strontium cerates, doped with neodymium and yttrium, respectively. It was shown that in the dry atmosphere, the oxygen index of $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ was higher than that expected in a wide range of temperatures and partial pressures of oxygen. At the same time, under similar conditions, the oxygen index of $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ was close to

the expected value of 2.975. The excess oxygen found in $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ was called superstoichiometric by the authors, and its appearance was attempted to be explained by the structural features of this oxide. In [9], we obtained confirmation of the presence of superstoichiometric oxygen in barium cerate doped with neodymium. Later we showed that superstoichiometric oxygen is present only in barium cerate doped with Nd, and absent in barium cerate doped with Sm, Gd or Y [10]. Along with this, it was noticed that the amount of water in the sample, doped with neodymium, was less than in the samples with other dopants. In [11], it was concluded that Nd in these compounds can show a mixed valence of +3 and +4, and when annealing of the neodymium doped barium cerate in the oxygen containing atmosphere, part of the trivalent neodymium is oxidized according to equation (2), reducing the concentration of oxygen vacancies:



As the temperature rises in a reducing atmosphere, neodymium is reduced to Nd^{+3} state. Obviously, reduction of Nd^{+4} should be accompanied by the release of oxygen in the temperature range of reduction, as observed in the thermal desorption experiments. At the same time, the amount of superstoichiometric oxygen in the neodymium doped barium cerate should be proportional to the amount of tetravalent neodymium in it.

The obtained regularities of the effect of irradiation with low and high energy ions of inert gases on thermal desorption of oxygen and water molecules from $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ can be explained by the change in Nd^{3+}/Nd^{4+} ratio in barium cerate during irradiation.

Thus, the revealed increase in the amount of desorbed oxygen after low-energy irradiation probably indicates the increase in the proportion of neodymium in the 4+ state in the irradiated sample. Apparently, this can be explained by the fact that low-energy irradiation leads to a significant increase in concentration of oxygen vacancies, which, in turn, leads to the increase in the equilibrium constant of the quasi-chemical equation (2) and, as a result, the concentration of Nd^{4+} . Since the amount of released oxygen practically does not depend on the type of ion, it can be concluded that under these irradiation conditions, the concentration of vacancies in the sample reaches saturation. The decrease in the concentration of Nd^{3+} should lead to the decrease in the concentration of protons in the

sample, which is observed in the thermal desorption experiment (Fig.6).

If $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ is irradiated with high-energy ions of inert gas, the observed decrease in the concentration of superstoichiometric oxygen (Fig.5) is probably caused by the decrease in the fraction of Nd^{4+} in the series Kr, Ar, Ne. The latter can be explained by the peculiarities of defect formation under irradiation with the high-energy ions, in particular by the fact that at high energies of the ions, electronic defects make a significant contribution to the Nd^{4+} fraction. The increase in the fraction of trivalent neodymium should be accompanied by the increase in the concentration of protons in the sample and, as a consequence, the increase in the amount of desorbed water (Fig.7).

CONCLUSIONS

The features of the effect of irradiation type on the state of the $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ surface are revealed.

It was shown that the irradiation of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ with electrons leads to smoothing of the irradiated surface relief, while electron irradiation of undoped $BaCeO_3$ led to formation of a small pyramidal structure on the irradiated surface of the complex oxide.

It was noticed that in case of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ irradiation with the high-energy ions of inert gases, the solid-phase transformations took place on the surface of $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$, and in the series Ne, Ar, Kr the surface of the composite oxide resembled the spherulite growth stages — nucleation, growth and formation of spherulitic crust.

According to the data of thermal desorption spectroscopy, a conclusion was made about the mechanism of influence of irradiation with heavy ions of inert gases of high and low energy on the state of the gaseous components in $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$. The mechanism is based on the features of defect formation under irradiation with the ions of different energies, which determine the Nd^{3+}/Nd^{4+} ratio in the $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ lattice and, as a consequence, the state of the gaseous components.

Study of the conducting properties of the irradiated $BaCe_{0.85}Nd_{0.15}O_{3-\delta}$ is in progress and the results will be reported later.

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