ELECTRON BEAM MODIFICATION OF BARIUM CERATES DOPED BY Nd, Sm AND Gd

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The perovskite proton conductors are the perspective materials for application as the working electrolyte in various electrochemical equipments: fuel cells, electrolyzers, hydrogen sensors, pumps and etc. [1]. Currently it is proposed to apply the radiation modification to improve the conductive properties of the perovskite proton conductors [2, 3]. The criterion of particles selection for modification of barium cerates is primarily the conservation of the cationic composition of these materials after irradiation and the following treatments, therefore the first step of radiation modification is the selecting the type of perovskites radiation exposure. Based on the analysis of literature data and the preliminary research activities performed by us we have made the conclusion about the appropriateness of selecting protons, oxygen ions and electrons for perovskites modification. This paper provides the results of studying the effect of electron irradiation on the structure and the properties of ceramic barium cerate.

The samples of barium cerate, un-doped and doped with neodymium, samarium and gadolinium (x=10%), were annealed in air at the temperature of 650°C and irradiated by electrons with the energy of E = 1.3 MeV and the beam current 10 мA in the accelerator ELV-4 of the INP RK up to the doses 1, 5 and 10 MGy. Preliminary the calculations were made to estimate the temperatures distribution in the samples of barium cerate under the irradiation by electrons with the energy of 1.3 MeV.

The structure and the properties of the barium cerate with various dopants are studied by the methods of X-ray phase analysis, scanning electron microscopy, atomic-force microscopy, thermodesorption and infrared spectroscopy.

According to the data of X-ray phase analysis it was established that un-irradiated barium cerate is characterized by the perovskite structure not depending on the dopant type. At the same time the surface state of the un-irradiated doped cerates significantly depends on the dopant type and characterized by the cellular structure, which develops to a considerable degree in the series neodymium - samarium - gadolinium. The surface relief is the alternation of oval "granules" of various heights.

The special attention is given to the study of the gas components state in this material, since it is important from the point of protons transport mechanism clarification and for assessing the chemical stability of the material and its activity with respect to carbon dioxide. The method of thermodesorption spectroscopy was used to reveal the peculiarities of water, oxygen and carbon dioxide molecular release from barium cerate depending on the dopant type. It was established that all three dopants are characterized by water release and the amount of water, desorbed from neodymium doped barium cerate is less nearly in 2 times than from cerates doped by Sm and Gd. And the desorption of molecular oxygen was observed only on neodymium doped barium cerate (fig.1).

The detected decreasing of the desorbed water amount in case of Nd compared with Sm and Gd points to decreasing of oxygen vacancies concentration, available for intercalation of hydroxyl groups. The reducing of oxygen vacancies concentration below the expected one for the fixed level of doping is possible in case of changing the valence state of dopant cation. The analysis of literature data have shown that neodymium can have the mix valence 3+/4+ in certain conditions, when samarium and gadolinium are characterized by stable valence 3+ [4]. Therefore in case of Sm and Gd cerate doping the dopant cations are introduced in the position «B» with formation of defects Sm'_{Ce} and Gd'_{Ce} and formation of x/2 oxygen vacancies in the cerate, which are filled with hydroxyl groups under annealing in air. In the process of thermodesorption experiment the OH-groups are removed from the lattice in the form of water under heating of barium cerate in the vacuum. In case of Nd, the latter is introduced in the position «B» in the form of trivalent and tetravalent ions and forms, correspondingly, two types of defects Nd'_{Ce} and Nd^{x}_{Ce} (Kreger-Wink notations), with reducing of oxygen vacancies concentration. The value of oxygen index exceeds the expected one. However in the course of thermodesorption experiment under heating in the vacuum the Nd^{4+} can transfer in the state Nd^{3+}, and the oxygen would leave the lattice, which can be observed in the thermo-desorption experiment. It is necessary to notice that almost no oxygen release was found from irradiated by electrons and unirradiated the undoped barium cerate (fig. 1,a) and only small amount of water was released from the samples (fig.1 ,b).

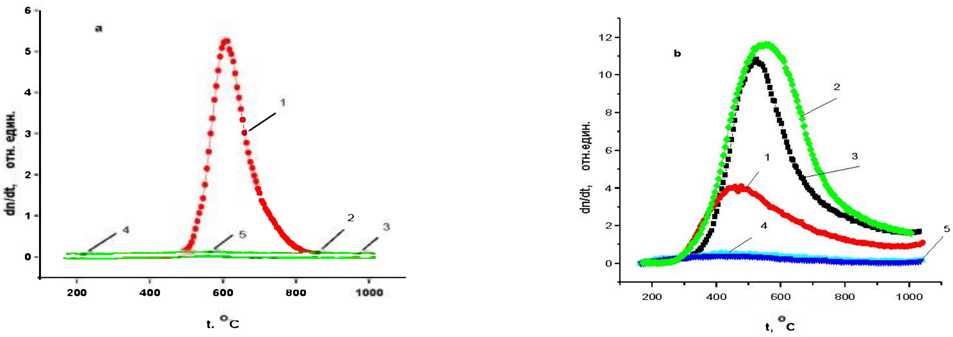

Figure 1 – *Oxygen (a) and water molecules (b) release from barium cerate with different dopant, annealed in air at the temperature 650°C: 1 – Nd; 2 – Sm; 3 – Gd; 4 – undoped; 5 – undoped + electron beam irradiation (10 MGy).*

The studies of the structure and properties of the irradiated barium cerate have shown that electron irradiation does not significantly effect on the structure of barium cerate and does not change its perovskite character. At the same time it is established that electron irradiation leads to significant relief smoothing of the irradiated surface and stimulates the formation of acicular structures on it. The size of the newly-formed structures (< 50 nm) allows us to make the conclusion about nano-structuring of surface under electron irradiation. These effects are displayed more clearly on the gadolinium doped cerate and strengthen with the irradiation dose growth (fig.2). Alongside with the relief change, electron irradiation promotes the surface cleansing from carbonate structures.

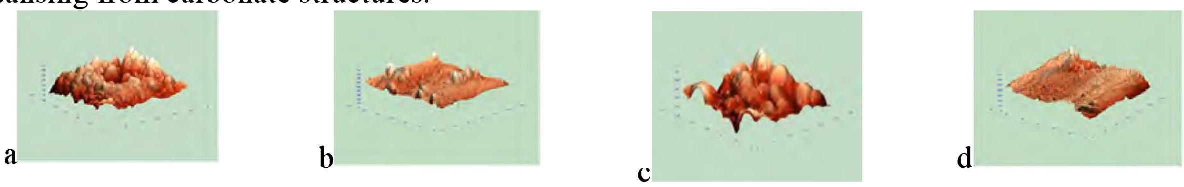

Figure 2 – *AFM images of barium cerate, un-doped (top) and doped with gadolinium (bottom): a, c – un-irradiated and b, d – electron irradiated cerates*

The paper is prepared under the support of the grant No.0609/GF by the Ministry of Education and Science of the Republic of Kazakhstan.

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