Particularities of Radiation Defect Formation in Ceramic Barium Cerate

I V Khromushin1, T I Aksenova1, T Tuseev2, K K Munasbaeva1, Yu V Ermolaev2, V N Ermolaev2, A S Seitov2

1 Institute of Nuclear Physics, 050032 Almaty, Kazakhstan
2 Kazakh National Technical University, 050013 Almaty, Kazakhstan

Email: khromushin@mail.ru

Abstract. The effects of irradiation with electrons, ions of noble gases (Ne, Ar, Kr) and oxygen on the structure and properties of neodymium-doped barium cerate have been studied using the methods of X-ray diffraction analysis, scanning electron and atomic force microscopy, thermal desorption spectroscopy. It was shown that irradiation by low-energy ions of noble gases stimulates the blistering processes on the sample surface, while the high-energy ions contribute to formation of the structures on the irradiated surface that resemble the various stages of spherulite growth. The similar structures were not observed in the case of irradiation with high-energy oxygen ions. According to the data on thermal desorption of water and oxygen molecules from the irradiated barium cerate it was supposed that irradiation by the noble gas ions promotes neodymium oxidation state change. It was noticed that the electron irradiation leads to the formation of the nano-sized acicular structures on the cerate surface.

1. Introduction
Recently it was noticed that the conducting properties of the solid-oxide electrolytes with the ABO3 perovskite structure can, in some cases, be improved by their radiation modification [1-4]. The results are explained by the oxygen vacancy formation as well as an increase in concentration and mobility of charge carriers caused by irradiation. However, the information on radiation modification of perovskite materials is still limited. The aim of this paper is to study the effect of different kinds of irradiation on the structure and properties of the neodymium-doped barium cerate.

2. Specimens and experimental procedure
The plates of the ceramic barium cerate doped with neodymium BaCe1-xNdxO3-x/2 (x=0.15) in the size of 10x5x1 mm were preliminary annealed in air at 650° C for 7 hours. Heavy ions irradiation was performed on the accelerator DC-60 in the Institute of Nuclear Physics in Kazakhstan (Astana city). All samples were irradiated to the same dose of 10¹⁶ cm⁻² and ion current was less than 1 μA. The samples were mounted on a stainless steel water-cooled flange. The sample temperature did not exceed 385K at irradiation. Irradiation was carried out in a chamber evacuated at a pressure of less than 1.33×10⁻⁴ Pa. The irradiation parameters are presented in the Table 1. The ion ranges and the vacancy formation rate were calculated using the SRIM - 2013 software [5].
Table 1. Sample irradiation parameters

| Ion type | High energy | Low energy |
|----------|-------------|------------|
|          | Energy [MeV] | Range [µm] | Vacancy/ion | Energy [keV] | Range [µm] | Vacancy/ion |
| O        | 28          | 13.0       | 1740        | O           | 40         | 0.080       | 243        |
| Ne       | 35          | 12.7       | 2700        | Ne          | 40         | 0.065       | 320        |
| Ar       | 70          | 13.2       | 8100        | Ar          | 100        | 0.080       | 800        |
| Kr       | 147         | 15.3       | 31000       | Kr          | 260        | 0.108       | 2500       |

Electron irradiation was performed on the electron accelerator ELV-4 in the Institute of Nuclear Physics (Almaty city) up to dose 10 MGy. The electron energy was 1.3 MeV providing the electron range in the material more than the sample thickness (1 mm).

The studies of heavy ion and electron effect on structure of doped barium cerate were performed using the X’Pert MPD PRO diffractometer with Cu–Kα1 radiation (λ=1,54060 Å). The morphology and chemical composition of local fragments of the specified surface areas were investigated using atomic force microscope (NT-MDT Probe Nanolaboratory Integra) and scanning electron microscope-microanalyzer (JSM-6490 LA (JEOL)) with energy dispersion extension. The special experimental setup with radio frequency spectrometer MX-7304 was used for gas thermodesorption study. This method allows to study gas desorption processes in vacuum while sample is heated with a definite rate. A personal computer with an Advantech PCI-1710HG module was used to select and control sample heating, choice of gas masses to be monitored, temperature and thermodesorption spectrum measurement. The sample heating rate was 42 K/min in all cases; pressure in working chamber was ~ 10⁻⁵ Pa.

3. Experimental results and consideration

The X-ray diffraction analysis showed that the structure of the non-irradiated barium cerate corresponds to the perovskite BaCeO₃ structure with an orthorhombic symmetry Pbnm. Fig. 1(a) shows the diffraction pattern of the non-irradiated neodymium-doped (x=0.15) barium cerate. It was found that the perovskite structure is maintained after irradiation with low-energy ions (O, Ne, Ar, Kr) and electrons. The amorphization of cerate and impurity inclusions (Fig. 1(b)) were detected in the case of barium cerate irradiation with high energy ions. It should be noted that degradation of the crystal lattice was also observed on the non-irradiating side of the ceramics, indicating that the changes in the oxide lattice, irradiated with high energy ions, occur up to the distances many times larger than the ion range in the material.

![Figure 1](image-url)
Fig. 2 illustrates SEM images of the surface morphology of the barium cerate irradiated with the low energy ions of neon (a), argon (b) and krypton (c), made at the same magnification. According to the Fig. 2, the blistering can be observed on the surface of cerate irradiated with ions of neon and argon; it can be observed more clearly in the samples irradiated with the neon ions. There was no blistering observed under irradiation of barium cerate with the krypton ions (Fig. 2(c)).

**Figure 2.** Electron micrographs of barium cerate surface irradiated with low energy ions of Ne (a), Ar (b) and Kr (c) to the dose of $10^{16}\,\text{cm}^{-2}$.

Irradiation of barium cerate with the high energy ions of noble gases caused the changes resulting, apparently, from the solid phase structural transformations on the surface (Fig. 3), and in the Ne, Ar, Kr series the barium cerate surface resembled the stages of spherulite growth: nucleation (a), growth (cauliflower view) (b), formation of spherulitic cover (c). Irradiation of this material with high energy ions of oxygen did not cause such changes of the surface (Fig. 3(d)).

**Figure 3.** Electron micrographs of barium cerate surface irradiated with high energy ions of Ne (a), Ar (b), Kr (c) and oxygen (d) to the dose of $10^{16}\,\text{cm}^{-2}$.

Data of atomic force microscopy (AFM) are in good agreement with the results of scanning electron microscopy and also indicate the solid-phase structural transformations on the surface of cerates under irradiation with high-energy ions of noble gases. Fig. 4(b) shows the AFM images of barium cerate surface after irradiation with high-energy krypton ions. After irradiation the surface relief looks "smoother" compared with the "bumpy" surface of the non-irradiated cerate.

**Figure 4.** AFM images of Nd-doped barium cerate non-irradiated (a), irradiated with Kr (147 MeV; $10^{16}\,\text{cm}^{-2}$) (b) and electrons (1.3 MeV; 10 MGy) (c)
The oxygen ions regardless of energy did not cause similar changes in the structure and state of the barium cerate surface, pointing to the peculiarities of defects formation in case of cerate irradiation with the ions of noble gases and oxygen. The revealed difference in the formation of the cerates surface structure under irradiation with high-energy ions of noble gases and oxygen is probably associated with their different solubility. It is assumed that in the first case the super-saturation of the material with the lattice defects takes place through their stabilization by the ions of noble gases with formation of the complexes "inert gas - vacancies". These complexes are characterized by high stability due to low solubility of noble gases in the materials. This is confirmed by the lack of noble gases release from the samples in thermal desorption experiments up to 1000°C.

In the case of high-energy oxygen ion irradiation of cerate at the elevated temperatures, the equilibrium concentration of the defects should be much lower. Indeed, the solubility of oxygen in cerate is significantly higher and under irradiation at elevated temperatures the oxygen may leave the material as a result of its diffusion to the surface and subsequent desorption. In this case, stabilization of the defect structure does not occur and the major part of defects, formed by irradiation, is annealed during irradiation.

Electron irradiation, as noted earlier, did not cause any changes in the perovskite structure of cerate; however, it resulted in smoothing of the surface relief. The peculiarity of barium cerate surface changes after electron irradiation is the formation of small pyramidal (acicular) structure (Fig. 4(c)) on it. The maximal height of the individual "pyramids" was about 50 nm; the "pyramids" effect was observed more clearly with the increase of the radiation dose. Dimensions and alternation of the newly formed structures suggest that electron irradiation promotes the nano-structuring of the cerate surface.

The studies of the processes of gases thermal desorption from the irradiated doped barium cerate indicate the dependence of these processes on the type and energy of ions. It is shown that the oxygen release was not observed from Nd-doped barium cerate irradiated with high-energy neon ions. (Fig. 5(a)).

![Figure 5](image-url)  
**Figure 5.** Oxygen (a) and water (b) release from Nd-doped barium cerate, non-irradiated (1) and irradiated with high-energy ions of Ne (2), Ar (3) and Kr (4) up to the dose $10^{16}$ cm$^{-2}$.

However, the increase in the amount of desorbed oxygen was observed with the increase of ions energy and mass, but the amount of oxygen released from the irradiated materials in all cases was less than from the initial ones (Fig. 5(a)). At the same time, in the spectra of water molecules release we observed the opposite picture compared with oxygen, i.e. the amount of the desorbed water decreased with the increase of ions energy and mass, but in all cases it was larger than that from the non-irradiated cerate (Fig. 5(b)). In addition, the low-temperature shoulder was observed in the spectra of water caused probably by the release of the physically adsorbed water.

Irradiation of barium cerate with low-energy ions of noble gases, in contrast to high-energy ions, called a significant increase in the amount of desorbed oxygen and the simultaneous decrease in the amount of desorbed water (Fig. 6(a, b)), and this effect was practically independent of ion mass and energy.
Figure 6. Oxygen (a) and water (b) release from Nd-doped barium cerate, irradiated with low-energy ions: 1 – non-irradiated sample; 2 – after irradiation with the ions of Ne; 3 – Ar; 4 – Kr (10^{16} \text{cm}^{-2}).

This behavior can be explained as follows. In the study of oxygen non-stoichiometry in barium cerate doped with various dopants it was shown that the value of the oxygen index greater than the expected value of $\delta = 3 - x/2$ was observed on the neodymium doped barium cerate [6, 7]. The analysis of the experimental results and their comparison with literature data allowed the authors to conclude that neodymium in the cerate lattice has the mixed valence of 3+/4+. This for the same degree of cerate doping with neodymium and other dopants, for example, Sm, Gd with the valence 3+, provides the visibility of the three-valent cation doping of less degree in the first case. According to [7] neodymium reduction takes place in cerate under the temperature increase. This, apparently, provides the release of the oxygen molecules from neodymium-doped barium cerate and reduced release of the water molecules in comparison with other dopants in the thermal desorption spectra. This pattern was observed in the thermal desorption spectra of water and oxygen from the doped barium cerate (Fig. 7).

Figure 7. Water (a) and oxygen (b) release from undoped (1) and doped with Nd (2), Sm (3) and Gd (4) barium cerate.

It can be seen that the oxygen release is observed only from neodymium-doped cerate, and the amount of desorbed water from the neodymium doped cerate, is less than from Sm and Gd doped cerates with the same degree of doping. This confirms the conclusions of [7] on the mixed valence of neodymium in cerate and its reduction under the temperature increase.

Considering above, the observed behavior of the thermal desorption spectra of the neodymium doped barium cerate samples irradiated with high-energy and low-energy ions of inert gases, can be explained by the change in the valence state of neodymium during irradiation.

Thus, irradiation with low-energy ions of inert gases under these conditions apparently makes a significant part of neodymium transfer to the tetravalent state, accompanied by the increased release of
oxygen and the reduced release of water compared with the non-irradiated cerate, and independence of the amount of released gases from the ions type.

Irradiation with high-energy ions of inert gases contrary causes the increase in the proportion of trivalent neodymium in the material. This, as expected, led to the reduced release of oxygen and the increased release of water from the irradiated materials in comparison to the non-irradiated ones. It should be noted that after irradiation with high-energy ions of neon practically the whole neodymium is in the trivalent state, as evidenced by the lack of oxygen release from cerate and the maximum release of water in the thermal desorption spectra.

The established patterns of the ions energies effect on the processes of oxygen and water thermal desorption are stipulated, apparently, by the peculiarities of defect formation in neodymium doped barium cerate under irradiation with low-energy and high-energy ions of inert gases. It should be noted that irradiation with oxygen ions and electrons had no appreciable effect on the desorption processes of oxygen and water molecules from the neodymium doped barium cerate.

4. Conclusion
The effects of electron and ion irradiation on the structure and properties of neodymium-doped barium cerate have been studied. Some peculiarities of irradiation type influence on the structure of doped barium cerates were revealed. On the analysis of gas desorption data it was supposed that irradiation by the noble gas ions promotes neodymium oxidation state change.

References
[1] Kim J-H, Tsuchiya B, Nagata S and Shikama T 2008 Effect of ion beam surface modification on proton conductivity of BaCe_{0.9}Y_{0.1}O_{3-δ} Solid State Ionics 179 1182-1186
[2] Kim J-H, Choi H and Shikama T 2011 Effect of Ar+ irradiation on the electrical conductivity of BaCe_{0.9}Y_{0.1}O_{3-δ} Applied Surface Science 257 8876-8882
[3] Khromushin I V, Aksenova T I, Tuseyev T, Munasbaeva K K, Ermolaev Yu V, Ermolaev V N and Seiott A.S 2013 Modification of barium cerate by heavy ion irradiation Advance Materials Research 781-784 357-361
[4] Tsuchiya B, Morono A, Hodgson E R, Nagata S and Shikama T 2008 Change in hydrogen absorption characteristic of SrCe_{0.95}Yb_{0.05}O_{3-δ} by electron beam modification Solid State Ionics 179 909-912
[5] Ziegler J F "Particle interactions with matter" http://www.srim.org
[6] Stevenson D A, Jiang N, Buchanan R M and Henn F E G 1993 Characterization of Gd, Yb and Nd doped barium cerates as proton conductors Solid State Ionics 62 279–285
[7] Oishi M, Yashiro K, Mizusaki J, Kitamura N, Amezawa K, Kawada T and Uchimoto Y 2008 Oxygen nonstoichiometry of perovskite-type oxides BaCe_{0.8}M_{0.1}O_{3-δ} (M= Y, Yb, Sm, Tb and Nd) Solid State Ionics 179 529-535