COMPARATIVE ANALYSIS OF PROCESSES OF PROTON INTERCALATION INTO CERAMIC AND SINGLE CRYSTAL SAMPLES OF BARIUM AND STRONTIUM CERATES

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Introduction

Taking into account lack of organic fuel and environment pollution an idea of hydrogen use for energy production in fuel cells is very attractive. In fuel cells water is product of oxygen and hydrogen reaction and free energy of the reaction is directly converted into electricity.

An efficiency of hydrogen energetic depends significantly on successful solution of whole row of problems such as hydrogen production, storage and transportation, search of high effective membranes-electrolytes.

Barium and strontium cerates are considered to be the perspective materials for use in fuel cells because of low gas permeability, high proton conductivity, rather high time and temperature stability [1].

Proton conductivity of these materials can be increased by their doping with low valence elements for creation of oxygen vacancies. Concentration of oxygen vacancies $\alpha = \frac{x}{2}$ depends on level of doping x.

In spite of active researches of proton conductivity many questions such as proton positions in the oxide lattices, hydrogen migration forms, stability of the oxides, oxygen behavior, influence of oxide synthesis technology on the properties of these materials are still under discussion.

In this work the results of comparative analysis of gas-solid exchange processes in barium and strontium cerates synthesized by different technologies are represented. Proton intercalation was reached as a result of sample annealing at different temperatures 650-750°C, oxygen and water vapor partial pressures. Then processes of gas release from the oxides into vacuum during sample heating were studied. Detail description of the method and experimental setup is given in [2].

Experimental results

It was found that processes of hydrogen and oxygen intercalation into oxide lattice depend on technology of samples synthesis, level of cation doping, gas partial pressure over samples during annealing.

An intensive water intercalation took place at doped barium cerates synthesized by ceramic technology even at room temperatures. Amount of water molecules desorbed from the single crystal samples was ~4.5 times lower then from ceramic ones of similar composition fig. 1.

It is necessary to notice that temperature of water desorption peak depends on water concentration in the samples and grows when water concentration in the samples increases.

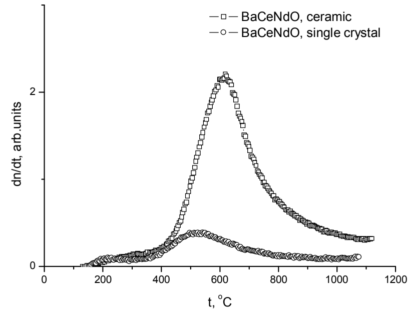

Fig.1. Water molecules release from doped barium cerates (10 %) after long exposition in air at normal conditions.

Similar behavior of water desorption spectra of single crystal samples was found earlier [2].

It is appeared that amount of oxygen intercalated into single crystal barium cerates approximately 5 times less then into ceramic samples annealed at similar conditions, and temperature of oxygen peak was lowered with increase of oxygen content in the samples fig. 2.

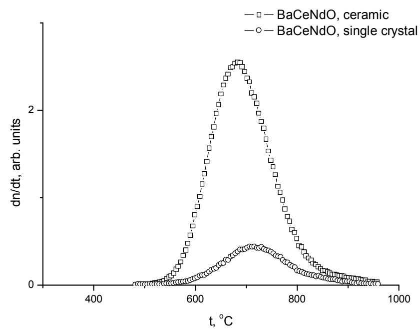

Fig.2. Oxygen release from single crystal and ceramic samples of doped (10 %) barium cerates annealed in air at 650 °C.

Unexpected fact was that undoped barium cerates could intercalate hydrogen even in the absence of oxygen vacancies. It was suggested that in case of undoped samples the hydrogen intercalation took place because of cerium mixed valence states $Ce^{4+}Ce^{3+}$ [3].

It is necessary to notice that high temperature phase transformation accompanied with oxygen release (fig. 3) take place in undoped single crystal samples annealed at 650 ^{o}C in different conditions.

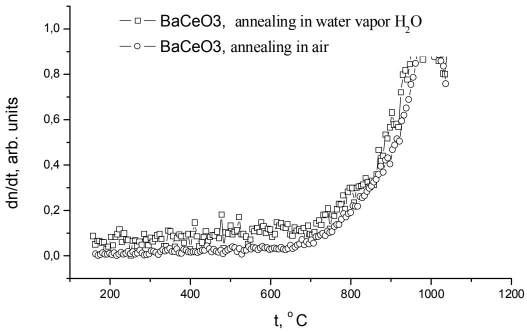

Fig.3. Oxygen release from barium cerates annealed in air and water vapor atmosphere at 650 ^{o}C.

Desorption spectra of undoped cerates synthesized by ceramic technology are more complex in comparison with spectra of single crystal samples. For example, five peaks of water and carbon dioxide release were found in desorption spectra of $SrCeO_3$ samples fig. 4. We arrived at a conclusion that these peaks caused by phase transformation in the oxides because of their temperature correlation.

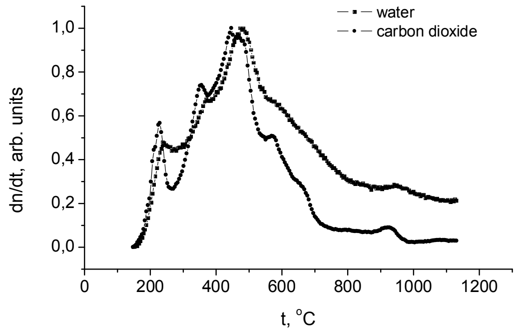

Fig.4. Oxygen and carbon dioxide release from ceramic samples of strontium cerates after long exposition in air at normal conditions.

So, it was shown that processes of hydrogen intercalation into these materials depend on technology of oxide synthesis. Presence of grain boundaries in ceramic samples, their lower density and homogeneity in comparison with single crystals are probably the main reasons of faster hydrogen intercalation in ceramic samples. Probably the same reasons are responsible for appearing of new phase transformations in ceramic samples.

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References

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