Proton conductivity of perovskite ceramics obtained by mechanical synthesis – optimization of the properties from the point of view of the application in electrochemical devices

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Introduction:

Perovskites are the crystalline solids of a relatively simple structure described by the formula ABX_3. Perovskites are a very large group of materials characterized by a number of interesting properties and therefore have a high application potential. The natural attribute of many of them is their structure rich in defects, particularly the presence of oxygen vacancies in the crystal lattice. The ability of absorption and dissociation of water molecules from the environment is characteristic of oxygen vacancies. As a result, a network of hydrogen bonds arises in the crystal lattice of perovskite and the proton conductivity is promoted. The process takes place at high temperatures (500 –600^{O}C and higher) and requires sufficiently moist environment, i.e. the presence of water vapor of proper partial pressure. The perovskites that show high intrinsic proton conductivity are e.g. $BaCeO_3$, $SrCeO_3$, $BaZrO_3$. The value of the proton conductivity is strongly influenced by the concentration of oxygen vacancies which depends on the proper choice of the elements the crystal is composed of. The oxygen vacancies concentration can be also changed by doping with other elements in the process of manufacturing. One of the methods for increasing the proton conductivity in perovskite ceramics is a reduction of the size of the ceramic grains up to nanometers in order to obtain the so-called nanoceramics. The effective surface area of the nanoceramic grains increases and at the same time the oxygen vacancies concentration increases resulting in the increase in the conductivity.

Scientific aim of the work and proposed research methods:

The aim of the work is the preparation of the perovskite nanoceramics characterized by high proton conductivity, destined for application in high-temperature electrochemical devices, as well as the investigation of their electrical properties. For preparation of the nanoceramics the modified conventional method will be used. The conventional method involves fragmentation of the substrates (usually the commercially available oxides of the elements included in the perovskite lattice) and the synthesis resulting from the heat treatment. The modification of the conventional method consists in the fragmentation of the substrates using the planetary ball mill which not only allows to get the ceramic grains of nanometer size but also to initiate the chemical reaction of the substrates through adequate choice of the parameters of the milling (mechanically triggered chemical reaction). In this work, barium zirconate and cerate ($BaCeO_3$, $BaZrO_3$) and also these compounds doped with e.g. Y (Yttrium) ions will be studied. The optimization of the method should allow to obtain different structures of the same ceramic material composed of crystal grains of lower resistance and more resistive grain boundaries. The proper ratio of these two resistances should influence the value of conductivity.

The basic measurement method for ionic conductors is the impedance spectroscopy. The Ferroelectric Department of the Institute of Molecular Physics PAS is equipped with a broad band impedance/dielectric spectrometer (Novocontrol Technologies) which allows measurements of electric properties of materials in frequency range $3\cdot10^{-6}$ Hz do $3\cdot10^{9}$ Hz and temperature -150 – 1200^{o}C. The obtained ceramics will be studied using the other spectroscopic methods (infrared radiation (IR), Raman, EPR, NMR). The morphology and quantitative composition will be investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively.