



Structural and electrical properties of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{M}_{0.1})\text{O}_3$, $\text{M} = \text{Y}, \text{La}$, solid solutions

Mirosław M. Bućko^{a,*}, Magdalena Dudek^b

^a AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Krakow, Poland

^b AGH University of Science and Technology, Faculty of Fuel and Energy, Poland

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ABSTRACT

The aim of the work was to study the structural and electrical properties of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ and $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{La}_{0.1})\text{O}_3$ solid solutions. The powders of different strontium content ($x = 0, 0.03, 0.05$ and 0.1) were prepared by a thermal decomposition of organo-metallic precursors containing ethylenediaminetetraacetate acid. Some parameters describing stability and transport properties of the perovskite structure, such as tolerance factor, specific free volume and global instability index, were calculated. It was found that the introduction of strontium into both solid solutions caused the increase of specific free volume and global instability index—these structures became a little less stable but, on the other hand, better ionic conductor. All samples were cubic perovskite and the substitution of strontium for barium caused the decrease of respective lattice parameters. Electrical conductivity measurements were performed by the d.c. four-probe method in controlled gas atmospheres containing Ar, air, H_2 and/or H_2O at the temperature from 300 to 800 °C. It was found that the conductivity depended on a chemical composition of the samples and the atmosphere. In general, the electrical conductivity was higher in wet atmospheres which contained oxygen, being in accordance with the model of a proton transport in the perovskite structure which assumed the presence of the oxygen vacancy. The solid solution containing 5 mol.% of strontium showed the highest conductivity and the lowest activation energy of conductivity regardless of the atmospheres.

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1. Introduction

There is a growing interest of MZrO_3 -based materials, where $\text{M} = \text{Ba}, \text{Sr}$, due to its possible applications as protonic conducting membranes in electrochemical devices such as hydrogen pumps, gas sensors, steam electrolyzers, solid oxide fuel cells (SOFC), separators or reactors [1–4]. In general, the $\text{BaZr}_{1-x}\text{Y}_x\text{O}_3$ or $\text{SrZr}_{1-x}\text{Y}_x\text{O}_3$ materials exhibited lower electrical conductivity as compared to $\text{BaCe}_{1-x}\text{Y}_x\text{O}_3$ or $\text{SrCe}_{0.9}\text{Y}_{0.1}\text{O}_3$, respectively, where: $0 < x < 0.2$. However, the chemical and mechanical stability of solid electrolytes involving yttria-doped barium or strontium cerates could be limited in the gas atmospheres involving CO_2 , SO_2 and moisture [5,6]. To improve the protonic conductivity of the zirconate materials, a structural modification can be performed. The model of proton migration in perovskites assumes the existence of the two equivalent sites for the proton between the adjacent oxygens in the B-sites, one of which can be occupied by the proton. It reveals the hopping mechanism of the proton changing O–H bond one after another and a distortion of the two neighboring BO_6 octahedrons is necessary

to make this process possible [7,8]. It was stated that proton conductivity in perovskite-type oxides is strictly connected with the differences between radii of the host and dopant ions and their electric charges and the amount of respective dopants [9–11]. There are many studies on the proton conductivity of barium zirconate solid solutions in which the B-site is modified, whereas the studies on the modification of the A-site are rather limited. Our previous work [12] proved that the introduction of 5 mol.% of calcium into barium zirconate solid solution, regardless of atmosphere, leads to the improvement of electrical conductivity compared to $\text{Ba}(\text{Y}_{0.1}\text{Zr}_{0.9})\text{O}_3$ sample.

This study is focused on structural and electrical properties of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ and $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{La}_{0.1})\text{O}_3$ solid solutions as proton conductors.

2. Experimental

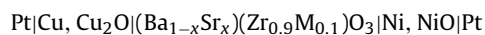
All powders were prepared by means of the polymer complex method with the use of versenate acid (ethylenediaminetetraacetate acid—EDTA). The starting aqueous solutions were prepared by dissolving appropriate amounts of barium, strontium, zirconyl, yttrium or lanthanum nitrates (Merck, p.a.) in distilled water. However, as versenate acid's solubility in water is very poor, it was

* Corresponding author. Tel.: +48 12 617 35 72; fax: +48 12 617 24 93.
E-mail address: bucko@agh.edu.pl (M.M. Bućko).

dissolved in a concentrate solution of ammonia. The ammonium versenate solution was added dropwise into a vigorously agitated solution of the respective cation nitrates. During this operation some increase of turbidity was observed due to hydrolysis of the versenate acid. By fixing pH values at about 8 with concentrated ammonia, it led to dissipation of this turbidity. The amount (in moles) of introduced ammonium versenate exceeded by 10% of the total amount of cation moles. The solutions, after being stored for 24 h at room temperature, were dried at 250 °C. The solutions changed their tint while drying, from colourless through yellow to dark-brown, and at this stage a dense, viscous liquid was obtained (resin). By further drying it, this led to a disintegration of this resin, releasing significant amounts of gases and finally setting into a very porous and black solid body. The total drying time extended 12 h. The prepared precursors were initially calcined at 600 °C for 2 h in order to completely remove carbon and/or the rest of organic phases, and then at 1200 °C for 2 h. The powders were ground in the rotary-vibratory mill in dry isopropyl alcohol for 2 h using zirconia grinding media. Isostatic pressing at 250 MPa was used to compact the powders which were then sintered at 1600 °C for 2 h. The procedure described above allowed us to prepare samples with the following chemical composition $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$, where $x = 0, 0.03, 0.05$ and 0.1 . The samples are described in the text as B-ZY, B03S-ZY, B05S-ZY and B10S-ZY, respectively. The second sample series was $(\text{Ba}_{1-x}\text{Sr}_x)\text{Zr}_{0.9}\text{La}_{0.1}\text{O}_3$, where $x = 0, 0.05, 0.1$, which were mentioned in the text as B-ZL, B05S-ZL and B10S-ZL, respectively.

Some structural parameters, such as Goldsmith tolerance factor, t , specific free volume, SFV and global instability index, GII, describing the perovskite structure, were calculated using the SPuDS software package [13]. The phase composition of all powders and sintered bodies were identified by the X-ray diffraction analysis based on ICDD data base. XRD measurements were done using Panalytical X'Pert Pro system with monochromatic Cu K_α radiation. Lattice parameters of the identified phases were determined using the Rietveld refinement method.

The oxygen ion transference numbers of all samples were estimated from electromotive force (emf) measurements of the solid oxide galvanic cell:



where $M = \text{Y}$ or La (1)

The two-phase mixtures (Cu, Cu_2O) and (Ni, NiO) with the known equilibrium oxygen partial pressures were used to provide fixed oxygen potentials at the electrodes [14]. The procedure was practically the same as of that presented in the work of Kiukola and Wagner concerning solid oxide galvanic cells involving the cubic phase of the $\text{CaO}-\text{ZrO}_2$ solid solution [15]. The ionic transference numbers (t_{ion}) of the samples were determined basing on the emf values, (E_m) measured for the cell (1) and on the emf values (E_t), obtained for the same cell with a pure oxygen ion conductor, $\text{Ca}_{0.13}\text{Zr}_{0.87}\text{O}_2$ (13CSZ), as an electrolyte:

$$t_{\text{ion}} = \frac{E_m}{E_t} \quad (2)$$

The total electrical conductivity was measured by the d.c. four-probe method in the temperature range 300–800 °C in different gas atmospheres, such as synthetic air, argon and mixtures of 2 vol.% H_2 in Ar. These gases were dry or saturated with water vapour using the water bubbler (RH = 100% at 25 °C). Prior to electrical measurements the Pt electrodes (Heraeus) were applied at respective places of the rectangular samples.

3. Results and discussion

Tolerance factor, t , and specific free volume, SFV, are important structural parameters determining stability and symmetry of the

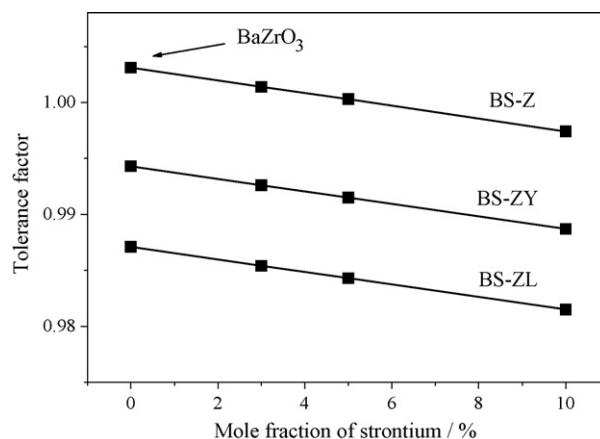


Fig. 1. Compositional dependence of the tolerance factor for $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{M}_{0.1})\text{O}_3$, $M = \text{Y}, \text{La}$, solid solutions.

perovskite structure as well as oxygen ions conductivity in such materials. The optimum t value was found to be around 0.96 due to balance between SFV and t in order to obtain maximum ionic conductivity [16]. The crystallographic analysis shows that the tolerance factor for pure barium zirconate is very close to unity, thus its cubic structure described by the space group of $Pm\bar{3}m$ is stable. Fig. 1 shows the changes of tolerance factors caused by the addition of strontium to the prepared solid solutions. All the structural factors were also calculated for $(\text{Ba}_{1-x}\text{Sr}_x)\text{ZrO}_3$, BS-Z, series as a reference. In each sample series a decrease of t value is observed regardless of the kind of the B-site dopant, yet the minimum t value is still over 0.97. For such value changes of the perovskite structure, e.g. transformation into the lower-symmetry lattice, are usually not observed. Such small changes can be the effect of mutual compensation of ionic radii changes—the smaller Sr^{2+} ($r = 132$ pm) for the larger Ba^{2+} ($r = 149$ pm) but the larger Y^{3+} ($r = 104$ pm) or La^{3+} ($r = 117$ pm) for the smaller Zr^{4+} ($r = 86$ pm). It is also shown that a substitution of the bigger lanthanum ions, when compared to the yttrium ones, for the zirconium ions caused larger changes of the tolerance factor. The specific free volume determines a possibility of oxygen ions and, indirectly, protons migration and thus their conductivity in perovskite materials. It was shown that good oxygen conductors were the perovskites with SFV values higher than 0.4 [16–18].

The substitution of yttrium or lanthanum for zirconium in BaZrO_3 structure causes the increase of the specific free volume when compared to pure BaZrO_3 , Fig. 2. Similar results are shown

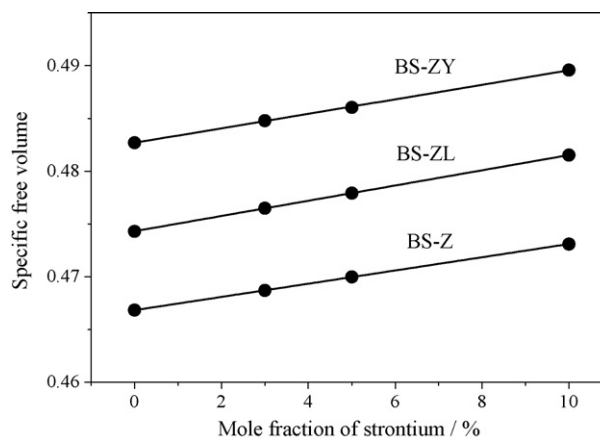


Fig. 2. Compositional dependence of the specific free volume for $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{M}_{0.1})\text{O}_3$, $M = \text{Y}, \text{La}$, solid solutions.

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