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Crystal structure and proton conductivity in highly oxygen-deficient $Ba_{1-x}La_x(In,Zr,Sn)O_{3-\delta}$ perovskites

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ABSTRACT

Results of studies of crystal structure (XRD method with Rietveld analysis), as well as transport properties (AC impedance method in dry and wet Ar atmospheres) are presented in this work for oxygen vacancy-disordered $Ba_{1-x}La_x(In,Zr,Sn)O_{3-\delta}$ with $\delta = 0.375$. La doping in the A-site, as well as Zr or Sn doping in the B-site resulted in stabilization of the cubic *Pm*–3*m* perovskite structure for all of the considered materials, despite having high In-content. Systematic studies of the electrical conductivity, performed in the 300–850 °C temperature range, allowed discussing the relationship between proton conductivity and structural parameters in the studied compounds. It was found that materials with a larger unit cell parameter possess higher proton conductivity in the whole temperature range, and, at the same time, the proton transference number for these compounds remains higher at higher temperatures.

1. Introduction

Proton-conducting perovskite-type oxides appear to be an interesting alternative to the oxygen ion-conducting materials for use as electrolytes in solid oxide fuel cell technology [1–3]. In 1980s and 1990s Iwahara et al. discovered proton conductivity in $(Ba,Sr)CeO_{3-\delta}$ oxides at high temperatures [4,5], which triggered the strong interest of research laboratories worldwide [6–12]. It is known that the presence of oxygen vacancies is required for incorporation of hydrogen (in a form of $OH^{\bullet}_{O}$ defects) into an oxide lattice, and that the enthalpy of hydration correlates with the weighted difference of the Allred–Rochow electronegativities between the B- and A-site cations [13]. The magnitude of the oxygen nonstoichiometry δ is typically in the range of 0–0.5 in $ABO_{3-\delta}$ perovskites. $Ba_2In_2O_5$ ($Ba^{2+}In^{3+}O_{2.5}$), at the high end of this δ range, has the brownmillerite-type oxygen vacancy-ordered and ion conductivity-disrupting structure below about 900 °C [14]. Appropriate modifications of the chemical composition of $Ba_2In_2O_5$ may lead to a formation of the oxygen vacancy-disordered structure, while at the same time a quite large value of δ can be maintained. Such materials, especially those exhibiting cubic symmetry, show remarkably high oxygen ion conductivity, and are considered as candidate solid electrolytes [15–18]. Interestingly, a large δ may also favor high proton concentration, as the maximum (theoretical) amount of the incorporated water molecules is equal to the value of δ. At the same time, an isotropic (cubic) structure favors a high rate of hydrogen migration in the lattice, which occurs as hopping between two adjacent oxygen anions [19–21].

Originally, the B-site substituted $(Ba,Sr)(Zr,Ce)O_3$ perovskites were studied as proton-conducting compounds [22]. The choice of the cations with different ionic radii was shown to have a profound effect on the degree of distortion from the cubic structure in these oxides, which was well described by Goldschmidt's tolerance factor $t_{Shannon}$. Considering the structural preferences of the cubic structure (i.e. large Ba^{2+} cations located at the A-site), the B-site substituted $BaIn_{1-y}M_yO_{3-\delta}$ ($M^{4+} = Zr, Sn$) materials, having high In content and a disordered oxygen vacancy sublattice, are of great interest [15,16,23,24]. These perovskites, containing only fixed-valence elements and having a large insulating energy gap, unlike the Ce-containing materials, are expected to exhibit a very low electronic component of electrical conductivity. Oxygen content in these oxides is strictly dependent on the level of doping, with $\delta = 0.5 - y/2$.

Introduction of lanthanide cations at the A-site of $Ba_2In_2O_5$ brownmillerite, e.g. La^{3+}, was shown to enhance proton conductivity, with maximum values exceeding $1 \cdot 10^{-5}$ S cm^{-1} at 400 °C for $(Ba_{0.9}La_{0.1})_2In_2O_{5.1}$ oxide, and diminishing for higher La content. This result was correlated with water uptake ability [25]. Mixed substitution at

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the A-site and B-site, which leads to general formula of disordered $(Ba_{1-x}Ln_x)(In_{1-y-z}Zr_ySn_z)O_{3-\delta}$ with $\delta = 0.5 - (x + y + z) / 2$, can be further used to tune the structural and ion conducting properties. We report here on proton conductivity in selected $Ba_{1-x}La_x(In,Zr,Sn)O_{3-\delta}$ perovskites, having a fixed value of $\delta = 0.375$, which was sufficient to achieve a disordered oxygen vacancy sublattice in a cubic structure. Contrary to most of the works published so far, we directly compare materials with the same oxygen nonstoichiometry, but with selection of various dopants, differing in ionic radius and electronegativity, which allowed clearly observing the relationship between these factors and proton conductivity.

2. Experimental

Perovskite-type oxides with fixed oxygen nonstoichiometry ($\delta = 0.375$) of the following compositions, $BaIn_{0.75}Zr_{0.25}O_{2.625}$ (BIZ), $BaIn_{0.75}Sn_{0.25}O_{2.625}$ (BIS), $Ba_{0.75}La_{0.25}InO_{2.625}$ (BLI), $Ba_{0.875}La_{0.125}In_{0.875}Zr_{0.125}O_{2.625}$ (BLIZ) and $Ba_{0.875}La_{0.125}In_{0.875}Sn_{0.125}O_{2.625}$ (BLIS) were synthesized by standard, high-temperature solid state reaction. Homogenized mixtures of respective oxides and carbonates were heated several times, with final sintering performed at 1420 °C in 5 N Ar (1425 °C for BLIZ).

The crystal structure of the samples was refined by the Rietveld analysis (GSAS/EXPGUI set of software [26,27]) of XRD data gathered using Rigaku D/MAX operating with the CuK_α radiation. Total electrical conductivity of the compounds was measured by the AC impedance technique, using Solartron 1260 Frequency Response Analyzer with 200 mV excitation voltage in the $1–10^6$ Hz frequency range. Data were collected in the temperature range of 300–850 °C in dry and wet Ar (ca. 3 vol.% H_2O). In order to examine the stability of the samples, the measurements were conducted initially in dry Ar, then in wet Ar, and again in dry Ar, during both, heating and cooling cycles. Generally, good reproducibility of the results was observed. Data in the following figures are shown as recorded during cooling. For the dry atmosphere data are presented for the 1st cooling. Analysis of the impedance spectra (fitting with the equivalent electrical circuit) was conducted using Scribner Associates Inc. ZView 2.9 software.

3. Results and discussion

3.1. Crystal structure

Prototypical $BaZrO_3$ and $BaSnO_3$ perovskites are characterized by the room temperature tolerance factor $t_{Shannon}$ slightly exceeding unity (1.004 and 1.018, respectively), and they exhibit a cubic structure. In these materials, however, there are no oxygen vacancies, and therefore, they cannot be used as proton conductors in wet atmospheres. On the other hand, highly-oxygen deficient $Ba_2In_2O_5$ brownmillerite is characterized by a lower value of $t_{Shannon}$ (0.979, assuming 10-fold coordination for Ba and mixed 4- and 6-fold coordination for In) and also the presence of the ordered oxygen vacancies up to about 900 °C in the undoped oxide [14]. With the intermediate compositions, it is expected that high values of δ may be maintained, with vacancies being disordered in a cubic-like perovskite structure.

As can be seen in Table 1, all of the synthesized materials exhibit an average cubic, *Pm*–3*m* structure at room temperature, despite their values of $t_{Shannon}$ smaller than 1, and high indium content (equal or exceeding 0.75 mol%). While tolerance factor was calculated by using two different sets of coordinations for the B- and A-sites; i.e., 6- and 12-fold for $t_{Shannon(6-12)}$, and 5- and 10-fold for $t_{Shannon(5-10)}$, both approaches lead to very similar results. Observation of the cubic structure is a direct proof that by the appropriate A- and/or B-site doping it is possible to synthesize oxygen vacancy disordered compounds. Table 1 shows that there is no linear dependence between $t_{Shannon}$ and the unit cell parameter *a*. Also, insignificant correlation was found between *a* and the relative free volume V_f [28], as well as the weighted difference of the Allred–Rochow electronegativities between the B- and A-site cations $\Delta\chi_{B-A}$. The only (expected) visible dependence is the one between parameter *a* and the sum of average radii of A- and B-site cations r_{6-12} (calculated using radii for 6- and 12-fold coordinations). It can be therefore stated that in order to obtain $(Ba_{1-x}La_x)(In_{1-y-z}Zr_ySn_z)O_{3-\delta}$ material with a larger unit cell parameter and volume, and maintain fixed δ at the same time, doping B-site with Zr, while keeping La at a low level, is the best choice.

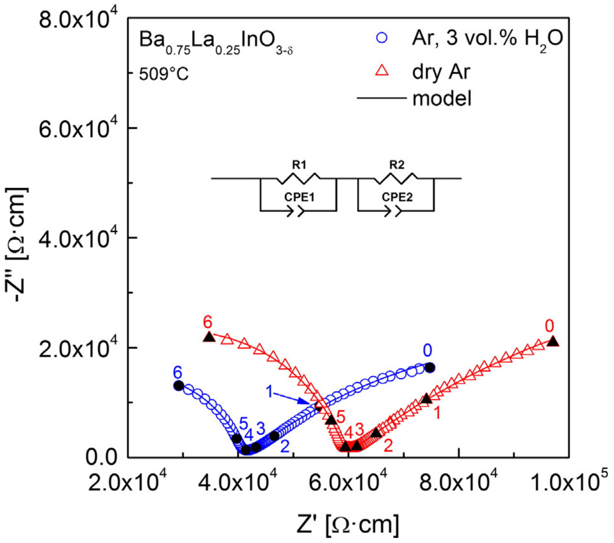

Fig. 1. Exemplary AC impedance spectra recorded for BLI material in wet and dry Ar at 509 °C together with used equivalent circuit. Given numbers next to the data points denote frequency exponent.

3.2. Transport properties

Fig. 1 shows exemplary AC impedance spectra measured at 509 °C for BLI material in wet and dry Ar atmospheres. Both spectra comprise two semi-arcs, of which the high-frequency arc can be interpreted as related to the bulk conductivity, while the low-frequency one is related to the charge transfer between a sample and the electrodes. Inset in Fig. 3 depicts an equivalent circuit used for the analysis of measurement. The visible change of the high frequency arc upon change of the atmosphere from dry to wet Ar is a proof that it originates from proton conductivity. A similar effect was observed for all the remaining samples. Fig. 2a depicts recorded temperature dependence of the electrical conductivity σ in dry Ar (300–850 °C range) for all of the studied compounds. Fig. 2b shows a similar dependence of σ measured wet Ar atmosphere.

Table 1
Structural and chemical parameters of the considered oxides (cubic *Pm*–3*m* space group).

Abbreviation	Unit cell parameter *a* [Å]	Sum of average radii r_{6-12} of A- and B-site cations	Tolerance factor $t_{Shannon(6-12)}$	Tolerance factor $t_{Shannon(5-10)}$	Relative free volume V_f [%]	Electronegativity difference $\Delta\chi_{B-A}$
BLI	4.1736 (1)	2.348	0.947	0.949	33.9	0.49
BLIS	4.1843 (2)	2.365	0.963	0.965	33.3	0.54
BLIZ	4.1907 (2)	2.369	0.962	0.963	33.6	0.47
BIS	4.1928 (2)	2.383	0.980	0.982	32.7	0.59
BIZ	4.2072 (2)	2.390	0.976	0.977	33.3	0.45

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