



The influence of anionic heterovalent doping on transport properties and chemical stability of F-, Cl-doped brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$



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ABSTRACT

The novel Cl-doped compound based on brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ was synthesized by the solid state method and its structure, thermal properties, hydration behavior and electrical properties have been investigated. The thermogravimetry, mass spectrometry and impedance spectroscopy methods were used for the characterization of the materials. The conductivity was measured at T, $p\text{O}_2$ and $p\text{H}_2\text{O}$ variation. The sample $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$ was capable to water uptake, however in comparison with $\text{Ba}_2\text{In}_2\text{O}_5$ and F-doped composition, the protonic conductivity was lower owing to the lower proton mobility. The changes in the chemical O–H bonding due to introduction of halogen in oxygen sublattice play an important role in the hydrogen-migration process. It was found that anionic heterovalent doping (F, Cl) of brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ leads to an increase in oxygen-ion conductivity and chemical stability against carbon dioxide.

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1. Introduction

Oxide materials that exhibit high ionic conductivity have attracted considerable attention owing to the wide range of applications (fuel cells, gas sensors, batteries) [1]. Amongst these uses, the fuel cells technology is a promising technology for future, to both clean energy generation, and the efficiency of electrical power [2]. One of the main problems of fuel cells technology is the search of highly conductive solid electrolyte with good chemical stability in oxidizing and reducing atmospheres. In recent years the medium temperature fuel cells (500–700 °C) are the most promising devices because of improving materials compatibility, reducing energy consumption and start-up time and extending the durability [3]. Protonic electrolytes based on perovskite complex oxides are appropriate materials for these temperatures [4]. The important factor, which limits the use of electrolytes, is a poor chemical stability in the atmosphere of carbon dioxide and water vapor [5]. The problem of competition between high proton conductivity and chemical stability does not allow creating long-term working electrochemical devices based on solid oxide protonic conductors. During the past decades, doping in A- and B-sublattices of the

perovskite-related structures has been the main strategy to search new phases with improved properties.

The anionic doping of perovskite-related matrix is a novel strategy permitting both to increase proton conductivity and to improve chemical stability. As an example, halogen (F, Cl and Br) doping effectively enhances chemical stability of gadolinium-doped barium cerate BaCeO_3 in CO_2 and H_2O steam [6]. Chlorine doping of samarium substituted barium cerate BaCeO_3 demonstrates a significant enhancement in chemical stability in the presence of CO_2 in the air without compromising its high proton conductivity [7].

Earlier, we have reported a new route for increasing oxygen-ion and proton conductivities by F-doping of brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ [8–11]. Brownmillerite can be described as a defective perovskite, in which the sixth oxygen atom of an ideal perovskite is absent. As a result, half of the oxygen octahedra are converted into tetrahedra. In this structure, a strict sequence of alternating layers of octahedra and tetrahedra is observed, which leads to ordering of oxygen vacancies. Brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ is characterized by the presence of an «order-disorder» phase transition, which is induced by the temperature. The disordering of oxygen vacancies occurs at the temperature of 925 °C, as a result of which orthorhombic symmetry changes to tetragonal symmetry [12]. The disordering leads to the increase in the oxygen-ion conductivity. The hydration of $\text{Ba}_2\text{In}_2\text{O}_5$ is accompanied by the formation of $\text{Ba}_2\text{In}_2\text{O}_4(\text{OH})_2$ phase, that

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is, almost one mole of water can be incorporated into a $\text{Ba}_2\text{In}_2\text{O}_5$ [13]. The presence of proton carries in the structure leads to the increase of the total conductivity values in the humid air [14–16].

Since the oxygen vacancy disordering in $\text{Ba}_2\text{In}_2\text{O}_5$ promotes an increase in electrical conductivity, various methods, such as cationic doping of barium [18–24] and indium [26–33] sublattices, as well as the oxyanion doping [17] were used for improving its transport properties. The systems with La^{+3} -doped barium sublattice [19–24] and with partial substitution of In^{+3} by Zr^{+4} , Ti^{+4} , Hf^{+4} and Mo^{+6} [25–33] were described as oxygen-ionic and protonic conductors. At the same time, we have recently shown that anionic doping strategy is an alternative to improve transport properties. It was proved that small F-concentrations (the solid solutions $\text{Ba}_{2-0.5x}\text{In}_2\text{O}_{5-x}\text{F}_x$ with $x = 0.1$) can increase the oxide-ion (mixed anion effect) and the proton conductivities [8–11].

However, the number of studied halogen doped ion-conducting oxide systems is still small and it is unclear how the mixed anions impact the mobility of main charge carriers (O^{2-} , H^+) and structural/chemical stability. For a better understanding the relationship between the doping effect and transport properties, we tried to make a comparison of different halogen-doped brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ with low dopant concentrations, and our new data were discussed with previously reported results. The new chlorine substituted brownmillerite of the composition $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$ was obtained and examined.

The introduction of a halide ion (Cl in our case) can be realized at the maintaining of the number of anionic sites and, accordingly, at the maintaining the maximum concentration of oxygen vacancies ($\text{ABO}_{2.5}\text{A}_2\text{B}_2\text{O}_5$) for the perovskite-related structure. The formation of vacancies in the barium sublattice occurs and charge neutrality is determined by $[\text{Cl}_\text{O}^-] = 2[V_\text{Ba}^{\prime\prime}]$. The defect reaction can be expressed as:

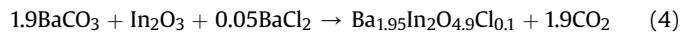
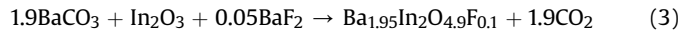


The solid state method of synthesis allows to control the concentration of halide ions by varying the barium oxide/barium chloride ratio, so it becomes possible to synthesize phases with a given concentration of oxygen vacancies.

This study demonstrates the role of anionic heterovalent doping for obtaining new oxide ion and proton conductors with potential applications in intermediate temperature SOFCs and opens up a new direction to design ion conductors with perovskite-related structure.

2. Experimental

The samples $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{F}_{0.1}$ and $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$ were prepared by a solid state method from preliminary dried stoichiometric amounts of high-purity powders of BaCO_3 (99.9999% purity, VEKTON, Ukraine), BaF_2 (99.99% purity, VEKTON, Ukraine), BaCl_2 (99.99% purity, REACHIM, Russia) and In_2O_3 (99.99% purity, REACHIM, Russia). The samples $\text{Ba}_2\text{In}_2\text{O}_5$ and $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{F}_{0.1}$ were prepared earlier, and here these compositions were synthesized for comparison. Following the methods, described earlier [8], all the samples were synthesized according to the same scheme. Prior to weighing, the starting materials were dried. The stoichiometric mixtures were mixed in agate mortar and then calcined (800 °C–1200 °C) with several regrindings. Reactions between starting materials can be expressed by the following equations:



The X-ray powder diffraction (XRD) measurements were made on a Bruker Advance D8 diffractometer with $\text{Cu K}\alpha$ radiation. The crystal structures of dried and hydrated samples were determined through Rietveld refinement using FULLPROF software.

Thermogravimetric analysis was carried out on a STA (Simultaneous Thermal Analyzer) 409 PC analyzer (Netzsch) coupled with a quadrupole mass spectrometer QMS 403 C Aëolos (Netzsch). For the preparation of hydrated forms of the specimens the powder samples were hydrated at slow cooling from 900 to 200 °C (1 °C/min) under a flow of wet air ($p_{\text{H}_2\text{O}} = 2 \cdot 10^{-2}$ atm). The cooling was performed down to a temperature not lower than 200 °C to avoid the appearance of adsorbed water. The hydrated forms of the samples were heated at the rate of 10 °C/min in a corundum crucible under a flow of argon.

The CO_2 stability of samples was determined on the powders that were exposed to the CO_2/air (1:1) mixture at 300 °C for 10 h. The treated powders were then examined by XRD.

The ceramics used for the electrical measurements were prepared by pressing disk-shaped samples at 250–300 MPa and sintering them at 1300 °C for 24 h in dry air. After polishing, the platinum paste electrodes were applied from both sides of the samples by painting and fired at 900 °C for 3 h. The *ac* conductivity of the samples (2-probe method) was measured using aZ-1000P (Elins) impedance spectrometer within the frequency range of 1–10⁶ Hz. The conductivity measurements were carried out under dry and wet air varying the temperature and partial oxygen pressure p_{O_2} . The bulk resistance was calculated from a complex impedance plot using the Zview software fitting. The “wet” air was obtained by bubbling the gas at room temperature first through distilled water and then through saturated solution of KBr ($p_{\text{H}_2\text{O}} = 2 \cdot 10^{-2}$ atm). The “dry” air was produced by flowing the gas through P_2O_5 ($p_{\text{H}_2\text{O}} = 3.5 \cdot 10^{-5}$ atm). The humidity of gases was measured by H_2O -sensor (“Honeywell” HIH-3610).

The measurements of the temperature dependencies of conductivities were performed from 1000 °C to 200 °C every 10–20 °C with a cooling rate of 1 °C/min and with 1 h equilibration times before each measurement. The conductivity also was measured at different partial oxygen pressures p_{O_2} at 500 °C. The p_{O_2} was controlled by electrochemical method. The oxygen pump (and sensor) from Y-stabilized ZrO_2 ceramic was used to control (and to measure) of p_{O_2} . Before the measurements the samples were equilibrated up to constant values of resistance for 3–5 h.

3. Results and discussions

3.1. Structure, thermal and chemical stability

Room temperature X-ray diffraction (XRD) results showed that the samples $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{F}_{0.1}$ and first synthesized $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$ were single phase (orthorhombic crystal system, space group *Ibm2*). The lattice parameters of investigated samples are presented in Table 1. XRD-pattern for $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$ refined

Table 1
The unit cell parameters and the unit cell volume of the samples $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{F}_{0.1}$, $\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$.

Sample	a(Å)	b(Å)	c(Å)	V(Å ³)
$\text{Ba}_2\text{In}_2\text{O}_5$	6.094(1)	16.740(0)	5.959(0)	607.90
$\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{F}_{0.1}$	6.074(2)	16.740(4)	5.959(3)	605.90
$\text{Ba}_{1.95}\text{In}_2\text{O}_{4.9}\text{Cl}_{0.1}$	6.084(3)	16.776(4)	5.959(0)	608.21

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