Effect of zinc doping on electrical properties of LaAlO₃ perovskite

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Abstract

New solid solution with the general formula of La₁₋ₓZnₓAlO₃₋₁/₂ was prepared by a solid-state reaction route. According to XRD, the crystal structure of LaAlO₃ is rhombohedral, while the solid solution possesses cubic symmetry. Homogeneity region of the solid solution La₁₋ₓZnₓAlO₃₋₁/₂ was narrow and limited to the maximum concentration of 5 mol. %. Computer simulations using crystallography and density functional theory approaches showed that LaAlO₃ has high energy barriers for O⁺-ion transport (>2.79 eV). These results are in good agreement with the low values of electrical conductivity obtained experimentally. The electrical conductivity of LaAl₁₋ₓZnₓO₂₋₁/₂ was measured by impedance spectroscopy in the temperature range of 200–1000 °C. The partial substitution of Al³⁺ by Zn²⁺ was found to increase the electrical conductivity by ~2 orders of magnitude. The electrical conductivity of doped phase LaAl₀.₉₅Zn₀.₀₅O₂₋₀.₇₅ as a function of oxygen partial pressure was measured, and the partial contributions (oxygen-ionic and electronic) were determined. It was found that the sample has mixed ionic and p-type electronic conductivity, while the electronic contribution increases with the rise of the temperature.

Keywords

perovskite
lanthanum alumina zinc
structure
ionic conductivity
modeling of ion transport
geometrical-topological analysis
Voronoi partition
BVSE-simulation
DFT-calculation

1. Introduction

During the past few decades, the perovskites have been used in various electrochemical devices and their properties have been well described. For example, these materials are promising electrolyte systems for solid oxide fuel cells (SOFCs). The general requirements for an electrolyte are high ionic conductivity, stability in both oxidizing and reducing environments, good mechanical properties and long-term stability. The electrolyte system, namely, yttria stabilized zirconia (YSZ) has been widely investigated for SOFCs, operating at 900–1000 °C [1]. In recent years, the focus of SOFC development has been on lowering the operating temperatures. Perovskites A²⁺B⁴⁺O₉, for example doped BaCeO₃ and BaZrO₂, are promising materials in this field due to their high proton conductivity. However, the presence of an alkaline earth component in the composition of perovskites A²⁺B⁴⁺O₉ can result in the formation of the corresponding carbonates [2–5], and thus to the degradation of the material.

A new direction of materials development is “alkaline earth elements free strategy”, that is, investigation of compounds not containing an alkaline-earth component. The modification of compounds with the general formula of A²⁺B³⁺O₉ is the most simple implementation of this approach [6–9].

The lanthanum aluminate LaAlO₃ (LAO) can be a promising perovskite material in this trend due to its high
chemical stability [10–13]. The systems based on LaAlO$_3$ can be good ionic or mixed conductors by adding suitable dopants [12]. Aluminates based on LaAlO$_3$ have such advantages as low cost of the initial materials, high thermodynamic stability due to the strength of Al–O bonds and wide $T$-$p(O_2)$ regions of ionic conductivity [12].

Complex oxide LaAlO$_3$ is a tolerant system to the different substitutions. The possibility of introducing various dopants into the La$^{3+}$ or Al$^{3+}$ sublattices of LaAlO$_3$ has been proven in several works. The substitutions of lanthanum by alkaline-earth elements (Ca, Sr, Ba) [7,11,14,15], aluminum by magnesium [7,15,16], and simultaneous co-substitutions into both sublattices [7–9,12,13,15,16] have been made. Thus, it was shown that the acceptor doping of LaAlO$_3$ produces a deficiency in the oxygen sublattice and, respectively, induces oxygen-ionic transport. It should be noted that the main substitutions are performed for the La-sublattice, and in this case the alkaline earth metal is the dopant, which reduces the chemical resistance of the material.

In this study we used ZnO as a dopant for several reasons: i) as an acceptor dopant, divalent Zn$^{2+}$ increases the concentration of oxygen vacancies in the perovskite-lattice; ii) in addition, due to the stable oxidation state, the doping will not lead to an increase in the electronic conductivity; iii) zinc belongs to the IIB group in the Periodic Table, it is not an alkaline earth element, the presence of which impairs chemical stability. Also, we assume that the introduction of zinc can reduce the synthesis temperature and will make it possible to obtain dense ceramics, as it was found in the works [17–20].

Although lanthanum aluminate has been a subject of many studies, the data of its electrical properties are not in good agreement. Thus, it is necessary to systematize the data on the electrical properties of LaAlO$_3$. In the present study, we also calculated migration paths and migration energy barrier for oxygen transport. The investigations of electrical properties of LaAlO$_3$ and Zn-doped at the B-site LaAlO$_3$ were performed.

2. Experimental

The LaAl$_{1-x}$Zn$_x$O$_{3-1/2x}$ (where $x=0$, 0.05, 0.1, 0.15, 0.33) samples were synthesized by solid state method. As initial reagents, preliminary dried oxides of the corresponding elements (99.99% purity, REACHIM, Russia) were used. Aluminum and zinc oxides were dried at 500 °C for 3 h to remove adsorption water. Lanthanum oxide was calcined at 1100 °C for 3 h to decompose the lanthanum carbonates LaOHCO$_3$ and La$_2$O$_2$CO$_3$ in accordance with [21].

The stoichiometric amounts of the oxides were weighed on an analytical balance with an accuracy of ±0.0001 g, mixed and ball-milled in ethanol. The synthesis was started at 700 °C, then the temperature was increased stepwise by 100 °C. All heat treatment steps were carried out with an isothermal holding time of 24 h, cooling with a furnace. After each heat treatment, the samples were milled in a planetary ball mill Pulverisette 6 (Fritsch, Germany) with ethanol and with using the zirconia milling bodies.

Single phase aluminate LaAlO$_3$ was obtained at 1250 °C. Single phase doped aluminate LaAl$_{0.95}$Zn$_{0.05}$O$_{3.975}$ was obtained at lower temperature 1200 °C. The synthesis of the samples LaAl$_{1-x}$Zn$_x$O$_{3-1/2x}$ ($x=0.1$, 0.15, 0.33) were continued at higher temperature 1300 °C. However, these samples were not obtained as the single phases; also, the sample with $x=0.33$ was melted at high temperatures.

Phase composition of the samples was determined by a powder X-ray diffraction method using a diffractometer D8 Advance (Bruker) with Cu Kα radiation in increments of 0.05° in the range of angles 2θ=10°–120° with exposures of 1s, a voltage of 40 kV and a current of 40 mA. The refinement of unit cell parameters was made using the FullProf software [22].

The surface morphology of the powder samples was studied by means of a high-end imaging desktop scanning electron microscope the Thermo Scientific “Phenom” Pha-ros (Phenom-World, Netherlands) with FOV: 912 μm, mode: 15kV - map, detector: BSD Full.

Multi-method modeling for the oxygen-ion conductivity for pure lanthanum aluminate LaAlO$_3$ was performed. We used a combined approach consisting of a crystallochemical analysis of geometric characteristics of free space in crystals, simulation of oxygen transport by the bond valence method (BVSE method) and quantum-chemical modeling of the ionic conductivity within the density functional theory (DFT) method.

The geometrical-topological approach is based on the Voronoi partition [23] and is implemented in the ToposPro software package [24]. Crystallochemical analysis reveals the geometric capabilities of the structure, i.e. a presence of wide voids and channels, which are accessible for anion migration. The criterion $R_{han}$ (an elementary channel radius) was determined for the geometrical analysis, which characterizes the presence of voids and channels in the structure, as described in [25]. $R_{han}$ describes the width of the bottleneck between two voids. This criterion is the sum of the radii of the working ions and the environment ions, taking into account the coefficient of ion deformation. This coefficient also takes into account the polarizability of the migration ion when passing through the channel. Based on the set of well-known oxygen conductors, we have chosen the coefficient of deformation for oxygen conductors of 0.8, so that $R_{han}$ was assumed to be equal to 1.73 Å.

The quantitative semi-empirical evaluation of activation energies of oxygen diffusion was conducted by the bond valence method. This approach is implemented in the SoftBV [26] and 3DBVS_MAPPER [27] packages. We use the SoftBV software package developed by the Adams group [26], due to its availability to users. The calculation procedure was carried out as described in [26]. We calculated
The migration energies for each species in the structure. This made it possible to reveal that ionic conductivity in LaAlO$_3$ is due only to oxygen anions. The method is not accurate enough, but allows a quick initial assessment of activation energies for ranking and, next, more precise quantum-chemical modeling of ion transport as described by Nestler et al. [28].

The DFT-calculations were performed for structure relaxation and calculations of oxygen migration energies. The VASP package [29] with the Nudged Elastic Band (NEB) method [30] were utilized. The GGA (generalized gradient approximations) exchange-correlation functional in the form of PBE (Perdew-Burke-Ernzerhof) [31] was applied. When optimizing the structure, the convergence thresholds were used $10^{-6}$ eV and $10^{-5}$ eV/$\AA$ for the energy and interatomic forces, respectively. The cutoff energy of plane waves in all calculations was taken equal to 600 eV and uniform Γ-centered k-point mesh for sampling the Brillouin zone with a reciprocal-space resolution of $2\pi \times 0.025$ Å$^{-1}$ was used. To minimize periodic interactions between neighboring cells, a $2\times1\times1$ supercell was used for NEB calculations. The optimized supercell lattice parameters are $a = b = 10.817$ Å, $c = 13.182$ Å, and $V = 1335.924$ Å$^3$. The convergence threshold for ion optimization was $10^{-5}$ eV/$\AA$ for NEB calculations. NEB calculations were carried out with a fixed supercell with parameters that corresponded to the optimized values.

The theoretical results were compared with the experimentally investigated electrical properties. For electrical measurements, the powder samples were formed into pellets with 10–12 mm in diameter and ~2 mm thickness by pressing at ~50 MPa. A solution of rubber in hexane was used as a plasticizer. The pellets were sintered at the temperature of 1250 °C (LaAl$_{0.99}$Zn$_{0.01}$O$_3$) and 1650 °C (LaAlO$_3$) for 24 h. Platinum electrodes in the form of finely dispersed paste mixed with an alcohol solution of rosin were applied to the preliminarily polished surfaces of the sintered tablets. The electrodes were burned for 2 h in air at 900 °C.

The relative density of the samples, determined by a hydrostatic method, was found to be 96% (LaAl$_{0.99}$Zn$_{0.05}$O$_3$) and 91% (LaAlO$_3$). For this experiment, dried pellets were soaked in kerosene ($\rho_k$=0.8 g/cm$^3$) for 24 hours. For the calculations, the mass of dried samples ($m_{dry}$) and the mass of pellets saturated of kerosene ($m_{sat}$) were used according to the equation:

$$W = \frac{m_{sat} - m_{dry}}{m_{dry}} \cdot \frac{\rho_{k,0}}{\rho_k}$$

(1)

The conductivity of the samples was characterized by an impedance spectroscopy technique. Measurements were performed by the two-probe method using a Z-1000 P (Elinx) impedance spectrometer under varying temperature (200–1000 °C) and partial pressures of oxygen ($P_{O_2} = 1 \times 10^{-20}$ – 0.21 atm). The oxygen partial pressure was measured and controlled by an oxygen sensor and a pump made of a solid electrolyte based on yttrium-stabilized zirconia ZrO$_2$(Y$_2$O$_3$). The obtained impedance spectra were analyzed using an equivalent circuits method and refined using Zview software [32].

3. Results and Discussion

3.1. Structural features of LaAlO$_3$ and morphology characterization

The XR-diffractogram of LaAlO$_3$ is presented in the Supplementary (Fig. S1). The obtained phase LaAlO$_3$ is characterized by the rhombohedral structure, in accordance with the JCPDS card №31-0022 and in agreement with literature data [6,8,10,33]. This is a slightly distorted cubic perovskite with the sp.gr. $\bar{R}3c$ and the unit cell parameters: $a = 5.408(5)$ Å, $c = 13.182(3)$ Å, $\gamma = 120^\circ$. Rhombohedral structure is stable modification of LaAlO$_3$ at room temperature. However, lanthanum aluminate exhibits a reversible phase transition from rhombohedral to cubic symmetry at heat treatment above 400 °C [34–36]. The cubic phase is unstable under room temperature. But in some studies, the cubic structure was stabilized at room temperature. A cubic modification was obtained by the mechanochemical [11] and the Pechini methods [15].

The morphology of the sample was investigated using scanning electron microscopy (SEM). Fig. S2a shows the SEM image of the powder sample LaAlO$_3$. The grains of the sample were small and had a size of ~1 μm.

Below we present the theoretical calculations of migration paths and a migration energy barrier for the oxygen conductivity for the rhombohedral phase LaAlO$_3$, obtained in this work.

3.2. Theoretical study of O$^{$2$-}$-ion conductivity

Voronoi partition was built for LaAlO$_3$ using the above described criterion $R_{han}$ in the ToposPro program. We have found a three-dimensional migration map for oxygen anions in the structure (Fig. 1).

The migration energy barrier for oxygen ion diffusion in LaAlO$_3$ is 1.844 eV according to the BVSE modeling, the corresponding energy profile is shown in Fig. S3. BVSE predict the formation of a three-periodic migration map.

The DFT results show that the oxygen diffusion map consists of two independent paths (Fig. 2a), while only one path (Path 1) is enough for the 3D oxygen diffusion.

Fig. 1 Migration map for oxygen anions in LaAlO$_3$ according to the geometrical-topological analysis. 3D migration map is highlighted in brown.
The DFT-NEB migration energy barriers for the paths 1, 2 are 2.86 and 2.79 respectively, the energy profiles are shown in Fig. 2b. It should be noted that the DFT migration energy values surpass the BVSE ones, similar to already described in the Nestler et al. [28]. It can be caused by strong O-O repulsion as well as many-body effects, which are counted in DFT and not considered in BVSE. But quantitatively both methods provide the similar outlook for oxygen diffusion map as shown in Fig. 3. The oxygen vacancy formation energy was evaluated as 6.15 eV/site according to the DFT data, see the Supplementary for more details. Because of the activation energy for diffusion is usually considered as a sum of the vacancy formation energy and the migration energy, we may conclude that LaAlO$_3$ should have a poor oxygen conductivity due to very high barriers.

As known from the literature, the energy involved in the process of migration from one site to the unoccupied equivalent site must be low, certainly less than about 1 eV [37]. The high quantitative values of the oxygen migration energy prove the necessity of doping perovskite in order to improve the conductive properties. Nevertheless, the implementation of a three-periodic migration map of O$^{2-}$-anion with the ability to migrate in different directions demonstrates the prospect of creating new perovskites with increased conducting properties.

Computer simulations using crystallochemistry and density functional theory approaches showed that LaAlO$_3$ has high energy barriers for O$^{2-}$-ion transport (>2.79 eV). However, computer simulations are carried out for ideal crystals, in according to the occupancy of all atoms at their sites. Therefore, the value of the experimental energy barrier can be less than the theoretical one due to defects and random vacancies in the real crystal.

3.3. Structural features of LaAl$_{1-x}$Zn$_x$O$_{3-1/2}$ solid solution and morphology characterization

The formation of LaAl$_{1-x}$Zn$_x$O$_{3-1/2}$ solid solution was controlled by XRD. Homogeneity region of the solid solution was controlled by XRD. Homogeneity region of the solid solution and morphology characterization was investigated by SEM and TEM. The samples with $x = 0.05$ and 0.1 were selected for further investigations. The XRD pattern of the single phase LaAl$_{0.95}$Zn$_{0.05}$O$_{2.975}$ is presented in the Supplementary (Fig. S2). The presence of impurities of the starting reagents.

The structures of LaAl$_{0.95}$Zn$_{0.05}$O$_{2.975}$ (LAZ9505) and LaAl$_{0.9}$Zn$_{0.1}$O$_{2.95}$ (LAZ91) can be refined as cubic perovskites with the unit cell parameters of $a = 3.785(2)$ Å and $a = 3.779(9)$ Å, respectively (a Pn$\bar{3}$m sp.gr.). The presence of zinc in the composition of solid solutions stabilizes the cubic structure of LaAlO$_3$.

Fig. 2a shows the SEM image of the powder sample LaAl$_{0.95}$Zn$_{0.05}$O$_{2.975}$. It can be seen that the sample has the same morphology as undoped sample. The grains of the sample had a size of ~1 µm and some grains aggregated to the clusters with the size of 10–20 µm.

3.4. Electrical measurements

Electrical properties were studied by the method of electrochemical impedance. As an example, for the sample of $x = 0.05$ the impedance spectra, recorded at different temperatures, were shown in Fig. 4a. The impedance plot is represented by one distorted semicircle started from the zero point. The impedance spectra were analyzed through the data fitting, using equivalent elementary circuits arranged in series consisting of one resistance ($R$) and one constant phase element (CPE) in parallel. The capacitance...
for these semicircles is determined to be $\sim 10^{-11}$ F/cm. The results of electrical measurements showed that there is no difference in the general view of the impedance spectra of doped and undoped samples. We can assume that this semicircle corresponds to a bulk response. We made this conclusion on the basis of the comparison with the data, presented in [11], since in many respects we have similar results: i) the average grain size of LaAlO$_3$ was found to be $\sim 1$ μm; ii) the capacitance for high-frequency semicircle is determined to be $\sim 10^{-11}$ F/cm; iii) the values of the conductivity of the undoped samples agree well (Fig. 4b).

The observed small second semicircle at low frequencies can be attributed to the grain boundary response. It should be said, according to literature data, the Nyquist plots are typical for the doped LaAlO$_3$ and exhibit, as usual, two semicircles – the bulk and grain boundary responses. However, the grain boundary resistance is very different from different works, and there is often a situation where the grain boundary semicircle is higher than the resistance of the bulk semicircle. For the investigated Zn-doped composition the observed second semicircle with specific capacitance of $\sim 2 \times 10^{-9}$ F/cm was small and was visible as separate semicircle at higher temperatures (Supplementary Fig. S5a). The capacity calculated for this semicircle correlated well with the data presented in [11], where the same second semicircle was assigned to the grain boundary response too. The evolution of impedance spectra for different temperature ranges is shown in Fig. S5 and Fig. S6.

The comparison of data on conductivity and density for the ceramics based on aluminate LaAlO$_3$ is presented in the Table S1. As seen, the reported conductivity values scatter in a wide range; this implies a strong influence of the phase and elemental impurities, porosity and microstructural characteristics.

Fig. 4b compares the temperature dependences of conductivities of undoped LaAlO$_3$, prepared in this work with literature data [5,6,10], solid solution LAZ9505 and composition LAZ91. The samples LAZ9505 and LAZ91 showed a high conductivity. The pure LaAlO$_3$ exhibits a low ionic conductivity due to the high binding strength of Al–O [12]. These data for LaAlO$_3$ are in good agreement with the literature data, presented in [11], although the reported conductivity values scatter in a wide range (Fig. 4b). Some literature data demonstrate a strong contribution of grain boundary resistivity to the total resistivity. For the reasons mentioned above, the bulk properties could not be determined and total contribution (bulk+grain boundary) has been presented [15]. At the same time, the high values of conductivity, measured in [7], are probably doubtful due to incorrect extrapolation of the large semicircle to the high frequencies.

Acceptor-doping of aluminum by zinc leads to an increase by 2 orders of magnitude of the total conductivity over the investigated temperature range. The energies of activation for LAZ9505 and LAO were 1.054 eV and 1.21 eV, respectively. This increase in conductivity of doped sample is due to creation of oxygen vacancies. The substitution of a divalent cation for a trivalent cation produces oxygen vacancy according to the quasichemical equation:
A comparison of the oxygen-ion conductivities of the investigated sample LaAlO$_3$ with an undoped composition LaAlO$_3$ as well as the most conductive composition of a Ca-doped sample, described in [11], is shown in Fig. 5b. As can be seen, doping in both cases leads to an increase in oxygen-ion conductivity, which is a result of the formation of oxygen vacancies (Eq. 3). However, the effect of increasing the oxygen-ion conductivity upon doping with Ca$^{2+}$ is greater. As it is known, two factors determine ionic conductivity, that is, defect concentration and mobility. For the case under consideration, with comparable defect concentrations, obviously, the mobility of oxygen vacancies is different. There are many factors that affect the mobility of oxygen vacancies [38], and in the general case, expansion of the cell volume weakens the metal-oxygen bonding and increases the oxygen vacancy mobility [39]. We believe that due to the smaller lattice parameter and, as a consequence of the smaller volume of the unit cell (V$_{cell}$= 54.225 Å), the ionic conductivity of the Ca-doped composition is lower than that of the La-doped composition (V$_{cell}$= 54.483 Å) [11].

The oxygen-ionic transport numbers $t_{ion}$ were calculated as a ratio of ionic conductivity to total conductivity $\sigma_{ion}/\sigma_{total}$. As an example, the Fig. 5c shows calculated data of $t_{ion}$ vs. $pO_2$ for LaAl$_{0.95}$Zn$_{0.05}$O$_{2.975}$ at 500 °C. It was shown that maximum values of $\sim$1 were reached at the partial oxygen pressures $pO_2 < 10^{-5}$ atm. The dependences of the oxygen-ionic transport number vs. $pO_2$ at different temperatures were similar. As can be seen, the sample in air had ion transport numbers of about 20%. These results show that studied phase is mixed ionic-electronic conductor under oxidizing conditions. As for the comparison of the ion transport numbers with other doped phases, based on LaAlO$_3$, it is known that an increase in the ion transport numbers can be achieved with an increase in the concentration of the acceptor dopant (due to an increase in the concentration of oxygen vacancies). For example, for the most conductive aluminate-based phases La$_x$Ca$_{1-x}$AlO$_3$, when calcium is introduced from 5 mol. % to 15 mol. %, the ion transport numbers in air increase from 18% to 55% [11]. Thus, for low concentrations of the dopants (5 mol. %), the ion transport numbers are comparable and do not exceed 20%. Unfortunately, Zn-substituted solid solutions with a high concentration of the dopant are not formed; therefore, such doping does not allow a significant increase in the ion transport numbers. However, it should be noted that Zn-doping significantly lowered the sintering temperature of ceramics (1250 °C), for example, Ca-doped ceramics were obtained at 1450 °C [11]. Probably, in the future, codoped phases may be of interest.

Fig. 5 Oxygen partial pressure dependence of conductivity of LAZ9505 at 500–900 °C (a); oxygen-ion conductivities of the LAZ9505, LAO and LCA8515 [11] samples (b); oxygen partial pressure dependence of oxygen-ion transport numbers of LAZ9505 at 500 °C (c).
For example, the codoping of Sr$^{2+}$ + Mg$^{2+}$ can significantly increase the conductivity, but high temperatures are required to obtain ceramics (Table S1). Therefore, the introduction of low concentrations of Zn$^{2+}$ into the B-sublattice of LaAlO$_3$ with simultaneous acceptor doping of the A-sublattice is a promising method for further investigations.

4. Conclusions

Zn-substituted LaAl$_{1-x}$Zn$_x$O$_{3/2}$ perovskites were prepared by solid state method. XRD analyses showed the formation of single phase after annealing at 1250 °C for pure LaAlO$_3$ and 1200 °C for LaAl$_{0.95}$Zn$_{0.05}$O$_{9.975}$ sample. It was found that lanthanum aluminate has a small homogeneity region ($\Delta x < 0.05$). LaAlO$_3$ structure can be refined as rhombohedral and solid solution LaAl$_{0.95}$Zn$_{0.05}$O$_{9.975}$ crystallized in cubic symmetry, so, zinc-doping stabilized the cubic structure of LaAlO$_3$.

For rhombohedral phase LaAlO$_3$ migration paths and migration energy barrier for oxygen transport were calculated. The material reveals very high energy barriers (2.86 and 2.79 eV) of O$^-$ ion transport and low conductivity. However, substitution by zinc was found to increase the electrical conductivity by 2 orders of magnitude compared to undoped LaAlO$_3$. Besides, sintering of Zn-doped phase at 1250 °C yielded dense ceramics with relative density of above 96%.

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https://journals.urfu.ru/index.php/chimtech/article/downloadSuppFile/4746/726.

Supplementary materials

The supplementary data are available online at:

https://journals.urfu.ru/index.php/chimtech/article/downloadSuppFile/4746/726.

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