




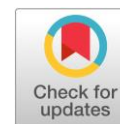
Synthesis and electrical properties of doped layered perovskites based on BaMInO_4 ($M = \text{Y, Gd}$)

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Abstract

Perovskite or perovskite-related structural materials are widely studied for their many functional properties. They can be used as components of electrochemical devices such as solid oxide fuel cells and electrolyzers. Layered perovskites can also be considered as promising materials for use in these devices. In this paper, the possibility of heterovalent (acceptor and donor) and isovalent doping of La and In sublattices of layered perovskites BaYLaInO_4 and BaGdLaInO_4 was made for the first time. The structure and electrical properties of these oxides were studied. Electrical conductivity values increase in the series BaYInO_4 – BaLaInO_4 – BaGdInO_4 . However, the doping is an unsuitable strategy for improving the electrical properties of BaYInO_4 and BaGdInO_4 oxides. Further search for highly conductive materials with the layered perovskite structure can be aimed at materials with a different composition of the cation sublattice.

Key findings

- The success of the doping strategy for layered perovskites $\text{Ba}(\text{Sr})\text{MInO}_4$ depends on the nature of the cations.

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Keywords

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1. Introduction

The complex oxides with high temperature protonic conductivity are actively studied due to their potential applications in electrochemical devices such as proton-conducting fuel cells (PCFC) and electrolyzers (PCEC) [1–8]. The design and production of such devices is part of the strategy of sustainable environmental development [9–16]. The most studied proton conductors are barium cerates-zirconates [17–24]. The barium zirconate crystallises in the classic perovskite ABO_3 structure. However, several years ago the possibility of proton transport was demonstrated for layered [25–26] and hexagonal perovskites [27–29]. Layered perovskites such as complex oxides materials based on nickelates lanthanides can be considered as efficient cathode materials [30–33]. Thus, the proton-conducting layered perovskites $\text{AA}'\text{BO}_4$ are very promising materials from the point of view of manufacturing PCFC/PCEC based on electrode and electrolyte with layered structure. The good

comparability between electrode and electrolyte materials with the same type of crystal structure can be expected.

Ionic conductivity for layered perovskites with the general formula $\text{AA}'\text{BO}_4$ were described for the compositions based on BaNdInO_4 [34–39], SrLaInO_4 [40–43], BaNdScO_4 [44], BaLaInO_4 [45], BaYInO_4 [38], BaGdInO_4 [38]. It was shown that method of heterovalent and isovalent doping can increase the ionic conductivity values by up to 1.5 orders of magnitude [25, 46, 47]. This paper first explores the possibility of heterovalent and isovalent doping of layered perovskites BaYInO_4 and BaGdInO_4 .

2. Experimental

The compositions BaYInO_4 , $\text{BaY}_{0.9}\text{La}_{0.1}\text{InO}_4$, $\text{BaY}_{0.9}\text{CaInO}_{3.95}$, $\text{BaY}_{0.9}\text{SrInO}_{3.95}$, $\text{BaY}_{0.9}\text{BaInO}_{3.95}$, $\text{BaYIn}_{0.9}\text{Ti}_{0.1}\text{O}_{4.05}$, BaGdInO_4 , $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$, $\text{BaGd}_{0.9}\text{CaInO}_{3.95}$, $\text{BaGd}_{0.9}\text{SrInO}_{3.95}$, $\text{BaGd}_{0.9}\text{BaInO}_{3.95}$, $\text{BaGdIn}_{0.9}\text{Ti}_{0.1}\text{O}_{4.05}$ were prepared by the solid state method. The powders of the starting reagents

BaCO₃, SrCO₃, CaCO₃, La₂O₃, In₂O₃, Y₂O₃, Gd₂O₃, TiO₂ were dried and used in stoichiometric amounts. The agate mortar was used for grinding. The compositions were calcined after each grinding. The annealing was carried out in the temperature range of 800–1300 °C with 100 °C step.

The phase identification of the obtained compositions was carried out using the Bruker Advance D8 Cu K α diffractometer.

The electrical conductivity was measured with an impedance spectrometer Z-1000P, Elins, RF. The investigations were carried out from 1000 to 200 °C with a cooling rate of 10/min under dry air or dry Ar. The dry gas (air or Ar) was prepared by circulating the gas through P₂O₅ ($p_{\text{H}_2\text{O}} = 3.5 \cdot 10^{-5}$ atm). The wet gas (air or Ar) was obtained by bubbling the gas at room temperature first through distilled water and then through a saturated solution of KBr ($p_{\text{H}_2\text{O}} = 2 \cdot 10^{-2}$ atm).

3. Results and Discussions

In this work, the isovalent doping of the lanthanum sublattice, BaM_{0.9}La_{0.1}InO₄ (M = Y, Gd), the heterovalent (acceptor) doping of this sublattice, BaM_{0.9}M'InO_{3.95} (M = Y, Gd, M' = Ca, Sr, Ba), and the heterovalent (donor) doping of indium sublattice, BaMIn_{0.9}Ti_{0.1}O_{4.05} (M = Y, Gd), were investigated. The XRD analysis showed that only matrix compositions, BaYLaInO₄ and BaGdLaInO₄, and the La-doped compositions, BaY_{0.9}La_{0.1}InO₄ and BaGd_{0.9}La_{0.1}InO₄, were obtained as single phases. Figure 1 represents the analysis of XRD data for these samples. The percentage of the target phase in the non-single-phase samples was 60–80, depending on the dopant.

The lattice parameters are provided in Table 1. The phases BaYInO₄ and BaY_{0.9}La_{0.1}InO₄ are indexed in the monoclinic symmetry (space group *P*2₁/*c*).

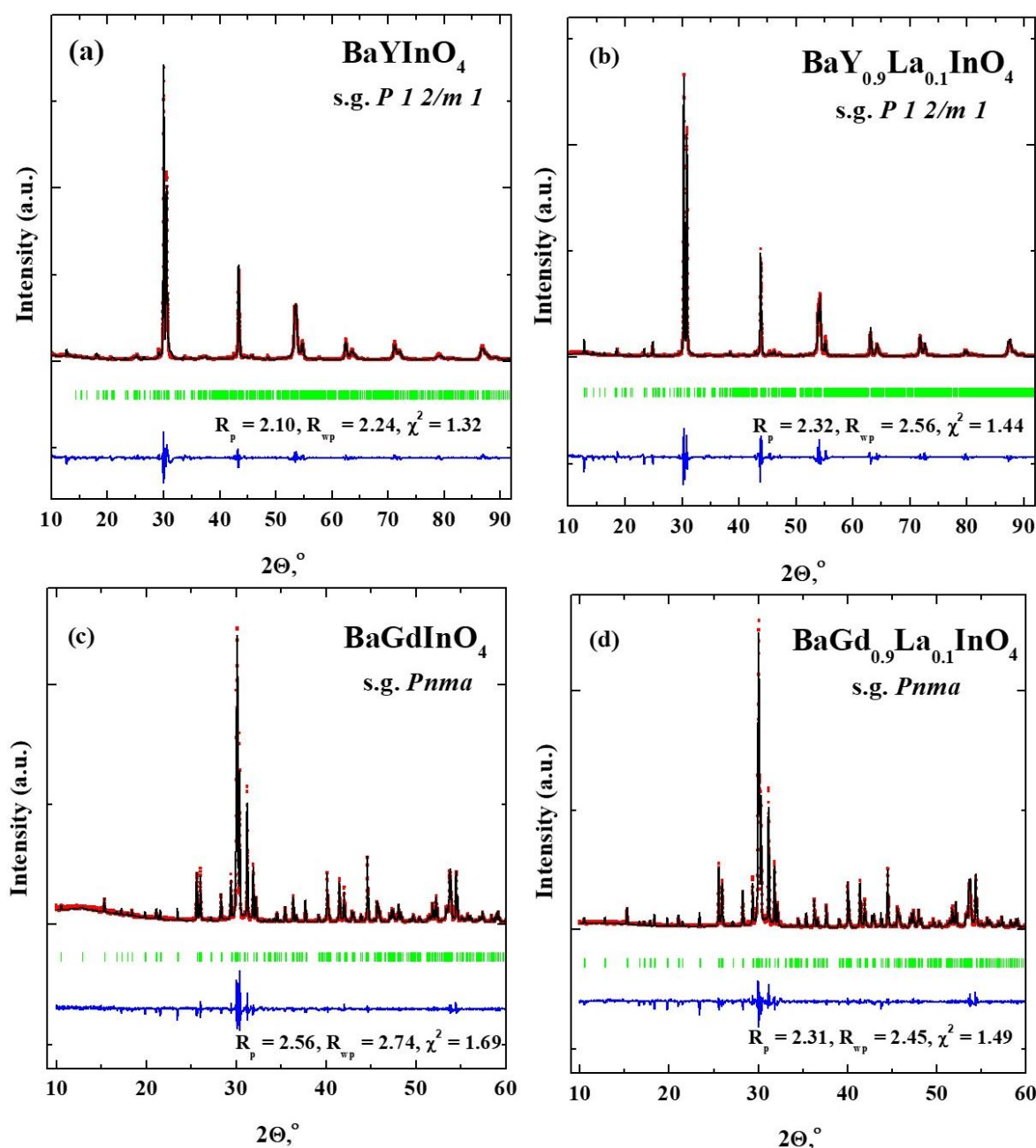


Figure 1 XRD patterns for the compositions BaYInO₄ (a), BaY_{0.9}La_{0.1}InO₄ (b), BaGdInO₄ (c) and BaGd_{0.9}La_{0.1}InO₄ (d).

The compositions BaGdInO_4 and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ are indexed in the orthorhombic symmetry (space group $Pnma$). The obtained data for the undoped compositions are in the good agreement with the previous reported data [38]. As can be seen, the introduction of lanthanum ions with slightly bigger ionic radii ($r_{\text{La}^{3+}} = 1.216 \text{ \AA}$, $r_{\text{Gd}^{3+}} = 1.107 \text{ \AA}$, $r_{\text{Y}^{3+}} = 1.075 \text{ \AA}$ [48]) leads to the increase in the lattice parameters and unit cell volume. Figure 2 represents the XRD data for the doped compositions based on BaGdLaInO_4 . The peaks belonging to unidentified impurities are marked. As we can see, the matrix phases BaYLaInO_4 and BaGdLaInO_4 have less tolerance to doping compared with BaLaInO_4 , SrLaInO_4 and BaNdInO_4 .

It is known that significant influence is exerted not only by the symmetry of the crystal and the ratio of the sizes of the cations, but also by the nature of the cations. We can suggest that the presence in the cation sublattice of combination of Ba/Y and Ba/Gd ions is not suitable for the formation of the oxygen defects (oxygen vacancy and oxygen interstitial) due to change in the energy of crystal compared with BaLaInO_4 .

The typical EIS-plots are presented in Figure 3. The conductivity values were calculated from the resistance values taken at the point of intersection of the high-frequency semicircle with the x-axis.

The temperature dependencies of the conductivity values for the compositions BaGdInO_4 and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ are presented in Figure 4a and Figure 4b, respectively.

Table 1 Lattice parameters and unit cell volume for the investigated compositions.

Compostion	a, b (Å)	c (Å)	V _{cell} (Å ³)
BaGdInO_4 [38]	13.7829	5.8835	10.6255
BaGdInO_4	13.7828	5.8833	10.6261
$\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$	13.8075	5.8947	10.6434
BaYInO_4 [38]	8.96	5.95	8.32
BaYInO_4	8.9661	5.9514	8.3253
$\text{BaY}_{0.9}\text{La}_{0.1}\text{InO}_4$	9.0083	5.9494	8.3435

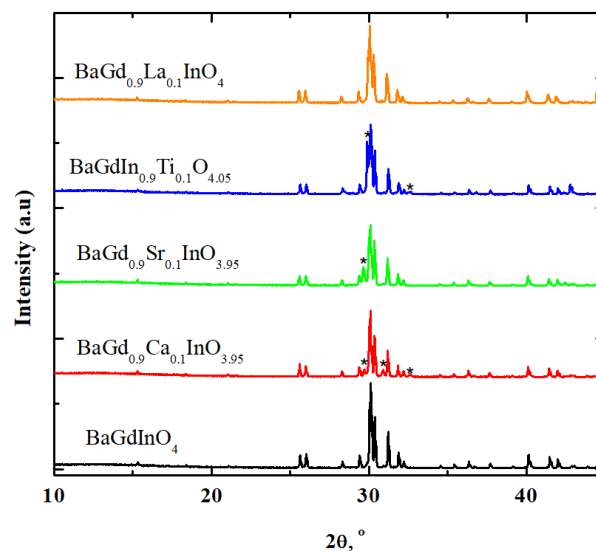


Figure 2 Comparison of XRD data for the compositions BaGdInO_4 , $\text{BaGd}_{0.9}\text{Ca}_{0.1}\text{InO}_{3.95}$, $\text{BaGd}_{0.9}\text{Sr}_{0.1}\text{InO}_{3.95}$, $\text{BaGdIn}_{0.9}\text{Ti}_{0.1}\text{O}_{4.05}$ and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$.

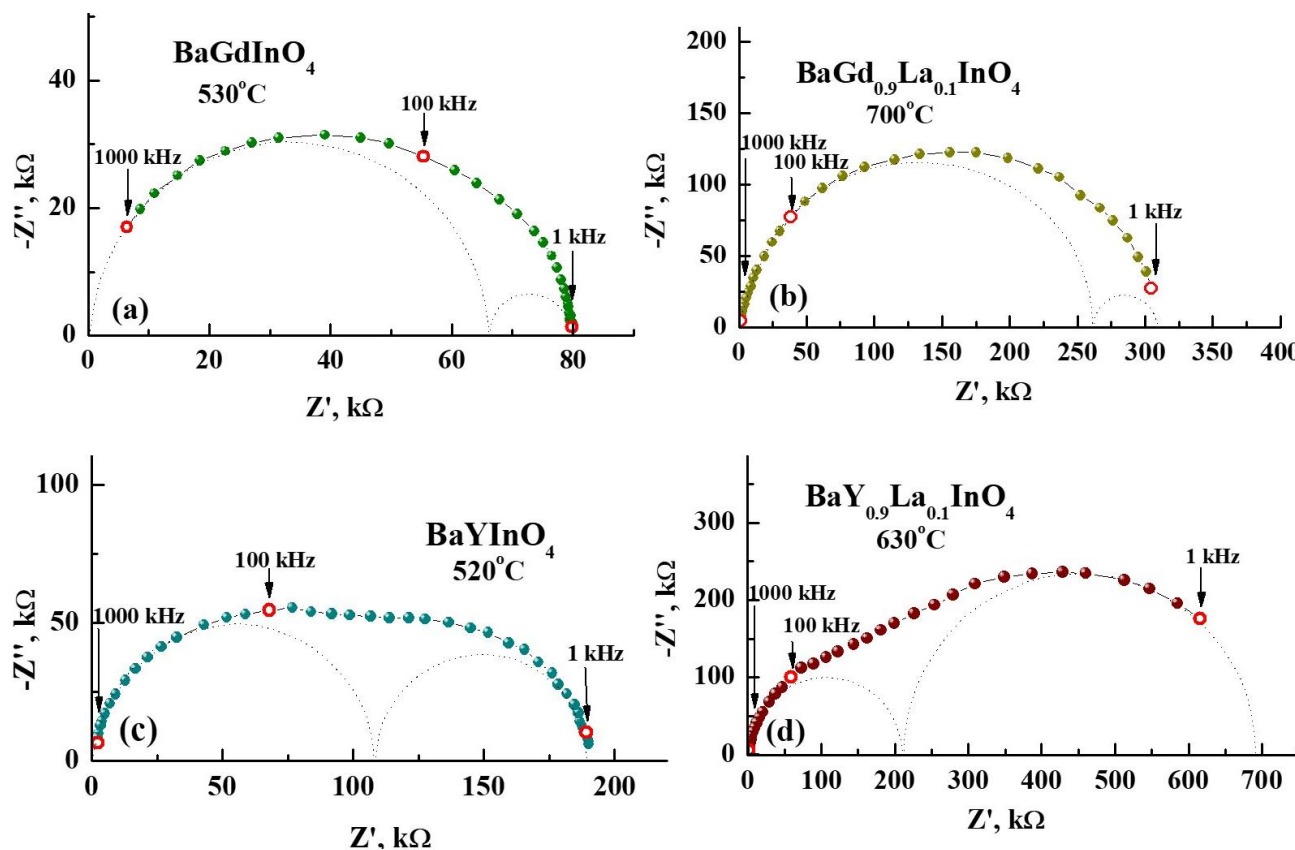


Figure 3 EIS plots for the compositions BaGdInO_4 (a), $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ (b), BaYInO_4 (c) and $\text{BaY}_{0.9}\text{La}_{0.1}\text{InO}_4$ (d).

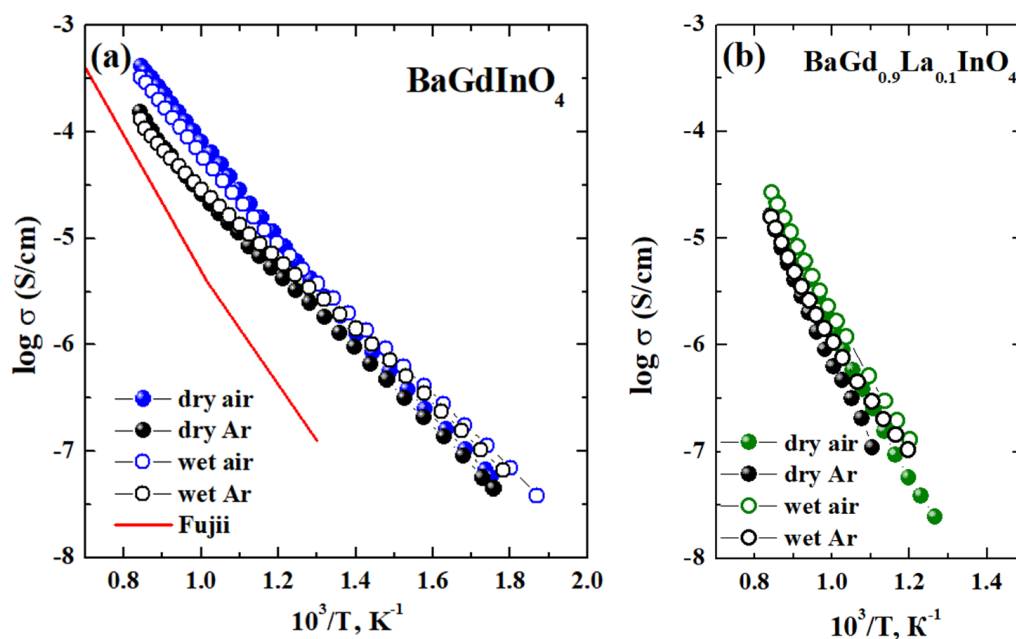
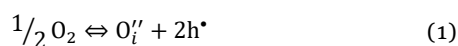
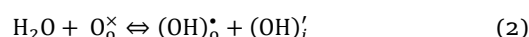


Figure 4 The temperature dependences of the conductivity for the compositions BaGdInO_4 (a) and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ (b) under dry (filled symbols) and wet (open symbols) conditions compared with data for BaGdInO_4 obtained by Fujii et al. (red line) [38].

The conductivity values for the undoped BaGdInO_4 compositions is higher than the data obtained by Fujii et al. [38]. Obviously, the reason for this is that the conductivity values in the work [38] were obtained in an atmosphere with uncontrolled humidity. The conductivity values under dry Ar ($p\text{O}_2 \sim 10^{-5}$ atm) are lower than those under dry air ($p\text{O}_2 = 0.21$ atm), indicating the hole contribution to the electrical conductivity:



Thus, the nature of the electrical conductivity under dry air is the mixed ionic-hole. The conductivity values under wet atmosphere is higher than under dry atmosphere which indicates the appearance of a proton contribution to conductivity:



The temperature dependences of the conductivity values for the doped $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ composition are described by the same regularities (Figure 4b). However, the comparison of conductivity values for the compositions BaLaInO_4 , BaGdInO_4 and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ (Figure 5) indicates that doping of BaGdInO_4 composition leads to the significant decrease in the conductivity values. At the same time, the Gd-containing composition BaGdInO_4 has higher conductivity values compared with La-containing composition BaLaInO_4 (about 0.5 order of magnitude).

Figure 6 represents the temperature dependences of the conductivity values for the compositions BaYInO_4 and $\text{BaY}_{0.9}\text{La}_{0.1}\text{InO}_4$. The discussion made earlier for the Gd-containing BaGdInO_4 and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ composition is also true for these the Y-containing compositions.

The conductivity values for all considered samples under dry air condition are presented in Figure 7. As we can see, among perovskites $\text{AA}'\text{BO}_4$ electrical conductivity

values increase in the series BaYInO_4 – BaLaInO_4 – BaGdInO_4 . In other words, Gd-containing composition is the most conductive among these matrix compositions. However, the doping is non-suitable strategy for the improving the electrical properties of this composition. The heterovalent (both acceptor and donor) doping does not allow obtaining single-phase compositions.

The isovalent doping leads to the decrease in the conductivity values. Further search for highly conductive materials with the layered perovskite structure can be aimed at materials with a different composition of the cation sublattice.

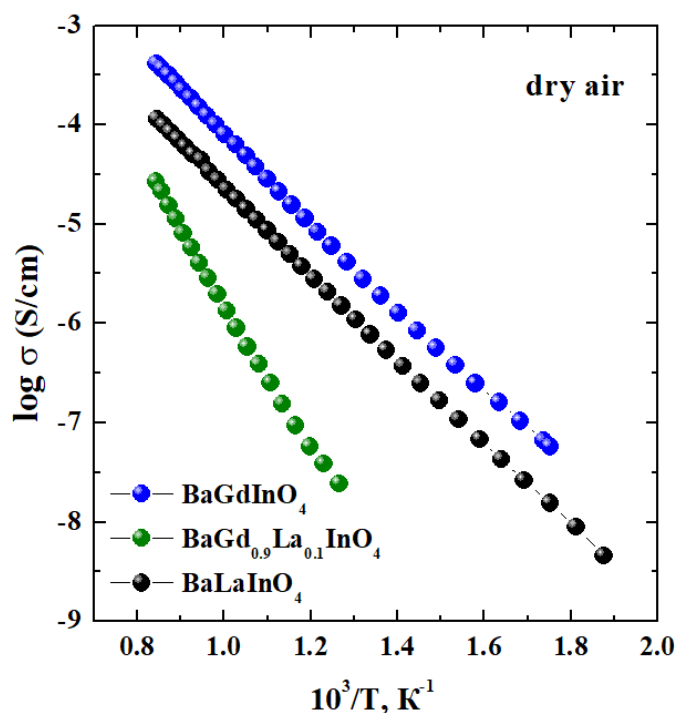


Figure 5 The temperature dependences of the conductivity for the compositions BaLaInO_4 , BaGdInO_4 and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$ in dry air.

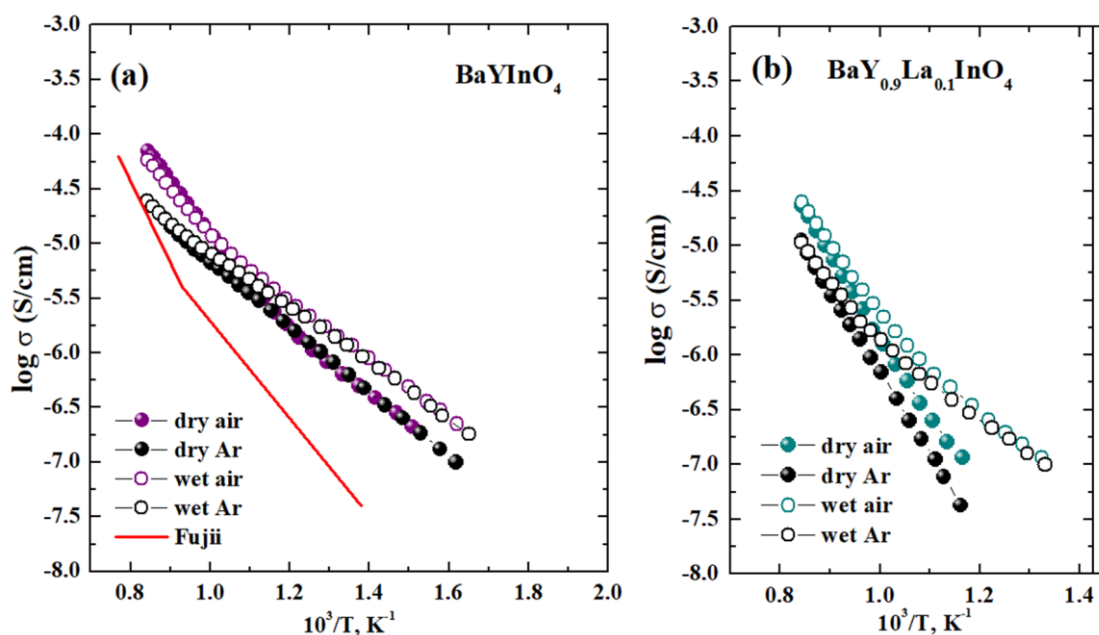


Figure 6 The temperature dependencies of the conductivity for the compositions BaYInO_4 (a) and $\text{BaY}_{0.9}\text{La}_{0.1}\text{InO}_4$ (b) under dry (filled symbols) and wet (open symbols) conditions compared with data for BaYInO_4 obtained by Fujii et al. (red line) [38].

4. Limitations

The main limitation is the difficulty in predicting the transport properties of complex oxides. The method of heterovalent and isovalent doping of cationic sublattices of layered perovskites was successfully applied for the compositions BaNdInO_4 , SrLaInO_4 , BaLaInO_4 with similar structure. However, for investigated matrix compositions this strategy was not successful.

5. Conclusions

In this paper, the possibility of heterovalent (acceptor and donor) and isovalent doping of La and In sublattices of layered perovskites BaYLaInO_4 and BaGdLaInO_4 was investigated for the first time. It was shown that both heterovalent (acceptor and donor) doping does not allow obtaining single-phase samples. The isovalent doping of Y(Gd) sublattice by La ions leads to the formation of single-phase compositions $\text{BaY}_{0.9}\text{La}_{0.1}\text{InO}_4$ and $\text{BaGd}_{0.9}\text{La}_{0.1}\text{InO}_4$. It was shown that doped compositions are characterized by lower conductivity values compared with undoped compositions. Among perovskites $\text{AA}'\text{BO}_4$ electrical conductivity increases in the series $\text{BaYInO}_4 - \text{BaLaInO}_4 - \text{BaGdInO}_4$. The nature of the electrical conductivity under dry air is the mixed ionic-hole conduction for all compositions. Further search for highly conductive materials with the layered perovskite structure can be aimed at materials with a different composition of the cation sublattice.

• Supplementary materials

No supplementary materials are available.

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 Investigation: A.B., M.D., D.K., R.B.
 Validation: A.G., N.T.
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 Writing – original draft: N.T.
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• Conflict of interest

The authors declare no conflict of interest.

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