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Oxygen-ion and proton conductivity in the $Ba_3InGa_2O_{7.5}$ complex oxide with incomplete oxygen sublattice

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Abstract

The $Ba_3InGa_2O_{7.5}$ complex oxide, possessing the perovskite-related structure with structural oxygen vacancies, was first synthesized by the solid state method. The phase was found to be characterized by monoclinic symmetry (sp. gr. P2/c) with the following unit cell parameters: $a = 7.942(1)$ Å, $b = 5.868(5)$ Å, $c = 18.201(6)$ Å, $\beta = 91.52(9)$. Comprehensive investigations of electrical properties were carried out; ceramic material based on the complex oxide was shown to be a predominantly ionic conductor in the temperature range 450–900 °C. The conductivity is due to oxygen-ion transfer in dry conditions and oxygen-ion and proton transfer in wet atmosphere. The proton conductivity value is $4.5 \cdot 10^{-5}$ S/cm, and the proton transport number is ~50% at 700 °C in wet air; at lower temperatures, proton transport becomes dominant. Prolonged treatment of the sample in water vapors below 450 °C leads to hydrolysis decomposition.

Keywords

complex oxide
perovskite-like structure
structural oxygen vacancies
solid electrolyte
oxygen-ion conductivity
proton conductivity

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Key findings

- The $Ba_3InGa_2O_{7.5}$ complex oxide has a $A_3BB'_2O_{7.5}$-type structure with structural oxygen vacancies.
- The $Ba_3InGa_2O_{7.5}$ is an oxygen-ion conducting solid electrolyte in dry air at 450–900 °C.
- The $Ba_3InGa_2O_{7.5}$ demonstrates oxygen-ion and proton conductivity in wet air with ~100% proton transfer at 500 °C.
- The phase undergoes hydrolysis decomposition in wet air at low temperatures.

Supplementary materials

1. Introduction

Proton conducting materials based on complex oxides are interesting for a practical use as functional components of electrochemical devices, including solid oxide fuel cells (SOFCs) [1–3]. The general research trend aimed at the reducing the operating temperatures of SOFCs, leads to an active search for oxide proton electrolytes with high proton conductivity at average temperatures of 500–700 °C. Perovskite-related complex oxides with a structural incompleteness of the oxygen sublattice can be considered as intermediate-temperature proton conductors. The presence of structural oxygen vacancies ensures an appearance of proton defects in the complex oxide structure due to the water uptake in wet conditions [4]; the proton defect transfer leads to the proton conductivity.

The most oxygen-incomplete type in perovskite-like family is the brownmillerite structure with the general formula $A_2B_2O_5$, where the B-cations occupy two polyhedral positions $[BO_6]$ and $[BO_4]$ with alternating octahedral and tetrahedral layers in the structure, and one oxygen position per formula unit is vacant $A_2B_2O_5(V_O)_1$. The $Ba_2In_2O_5$ barium indate with the brownmillerite structure is well-studied and described as oxygen-ion and proton conductor; solid solutions based on it remain in the attention focus of some researchers [5–9]. But it is interesting to find other complex oxides with structural oxygen vacancies, potentially exhibiting the proton conductivity.

If there are two different cations in B-positions in the $A_2B_2O_5$ formula in the ratio of 1:2, another perovskite-related structural type may be formed, such as $A_2B_{2/3}B'_{4/3}O_5 = A_3BB'_2O_{7.5}$, where A is an alkaline-earth metal ion and B and B' are octahedrally and tetrahedrally coordinated cations with 3+ charge, respectively. The structure assumes that some of the polyhedra [$B'O_4$] merge into [B'_2O_7], so the number of structural oxygen vacancies is lower than the nominal one. The structure is ordered by the B-sublattice (cations B/B') and by the oxygen sublattice (oxygen anions and structural vacancies O/V_O). There are detailed investigations of the crystal structure of the $A_3BB'_2O_{7.5}$ complex oxides with A = Ba^{2+}, B = rare-earth metal ion (REM), B' = Al^{3+}, Ga^{3+} [10]. The compounds are described in two structural forms: high-temperature α-phase (orthorhombic symmetry with sp.gr. Cmcm) and low-temperature β-phase (monoclinic symmetry with sp.gr. P2/c).

For the $A_3BB'_2O_{7.5}$-type phase with the formula $Ba_3YGa_2O_{7.5}$ and solid solutions based on it, a possibility of proton defects appearance and proton conductivity has been recently proved [11–13]. In the work [13] conductivity values of the $Ba_3YGa_2O_{7.5}$ was found to be practically independent of oxygen partial pressure (pO_2), which suggests that the compound is a predominantly ionic conductor both in dry and wet air. The complex oxide is oxygen-ion and proton conductor in wet air with the proton transfer domination at temperatures below 600 °C. The proton conductivity of $Ba_3YGa_2O_{7.5}$ was also described in the work [12] based on the difference in the electrical conductivity values measured in wet N_2 and dry N_2. Since the conductivity values are quite low, solid solutions based on the phase with various dopants were investigated to improve the properties [11, 12]. The isovalent substitution of the Ba^{2+} positions with the Sr^{2+} ions $Ba_{3-x}Sr_xYGa_2O_{7.5}$ ($0 \le x \le 3$) led to a decrease in the electrical conductivity due to a decrease in the volume of the unit cell [11]. But the solid solutions containing an excess of oxygen ions (interstitial oxygen defects) due to the heterovalent (donor-type) substitution of the Ba^{2+} positions with the La^{3+} ions or the Ga^{3+} position with the Ti^{4+} ions were found to show an increase in conductivity by about one order of magnitude [12].

It is interesting to obtain a compound that is isostructural to the $Ba_3BGa_2O_{7.5}$ phases (B = REM), but where the indium ion In^{3+} is in the B-position instead of a rare-earth element one. Note that there are studies into the Ga-substituted solid solutions based on barium indate $Ba_2In_{2-x}Ga_xO_5$ with $x \le 0.9$ [14, 15] and the individual phase Ba_2InGaO_5 (the In/Ga ratio 1:1) [16]. But the $Ba_3InGa_2O_{7.5}$ complex oxide with the In/Ga ratio 1:2 has not been previously described in the literature. The aim of the present investigations is to synthesize the $Ba_3InGa_2O_{7.5}$ compound and study its transport properties.

2. Experimental

The $Ba_3InGa_2O_{7.5}$ complex oxide was prepared by a solid-state method from stoichiometric amounts of barium carbonate $BaCO_3$ (99.9% purity), which was pre-annealed to remove chemisorbed water, and indium and gallium oxides In_2O_3 and Ga_2O_3 (99.9% purity). Starting reagents were ground in an agate mortar under ethanol. The annealing was carried out at temperatures 800, 1000, 1100, 1200 °C with intermediate regrindings. The total annealing time was 84 h.

The X-ray diffraction (XRD) studies were performed at room temperature by an XRD-7000 Maxima diffractometer (Shimadzu, Japan) with Cu Kα radiation (λ = 1.54 Å) in 2θ = 10–80°. XRD data were treated using the FullProf Suite software. The morphology and elemental composition of the sample were studied by a scanning electron microscopy (SEM) on a VEGA3 microscope (TESCAN, Czech Republic) equipped with an AztecLive Standard Ultim Max 40 system (Oxford Instruments Analytical, UK) for an energy dispersive X-ray analysis (EDX).

Thermogravimetric (TG) studies were carried out in heating mode from 50 to 900 °C (5 °C/min) in argon atmosphere using a thermoanalyzer TG STA 409 PC (NETZSCH, Germany). The composition of the released products was monitored using a mass spectrometric (MS) analyzer QMS 403C Aëolos (NETZSCH, Germany). Initially hydrated samples were used for the analyses. The hydrated samples were obtained by slow (1 °C/min) cooling from 900 to 500 °C (partially hydration) or 250 °C (fully hydration) and holding at 500 °C or 250 °C for 3 h in wet atmosphere ($pH_2O = 2\cdot10^{-2}$ atm).

Ceramic samples were formed as pellets by a cold pressing method and sintered at 1200 °C for 10 h. For electrical properties investigations the bases of the pellets were coated with a platinum paste and annealed at 900 °C for 1 h to get Pt-electrodes. The electrical conductivity was measured by impedance method in the frequency interval 100 Hz – 3 MHz at various temperatures (500–900 °C) and oxygen partial pressures ($pO_2 = 10^{-5}$–0.21 atm) in dry and wet air using a Z-3000 impedance spectrometer (Elins, Russia). The obtained impedance spectra were analyzed using an equivalent circuits method and refined using Zview software.

The wet atmosphere was provided by air bubbling through a saturated solution of potassium bromide ($pH_2O = 2\cdot10^{-2}$ atm). Dry atmosphere was obtained by air circulation through powders of calcium chloride and phosphorus pentoxide ($pH_2O = 3\cdot10^{-5}$ atm). To prevent carbonization of the ceramics, carbon dioxide was preliminarily removed with a 30% solution of sodium hydroxide from wet air or with solid sodium hydroxide from dry air. The humidity of the atmosphere was controlled using a sensor HIH-3610 (Honeywell, USA).

The oxygen partial pressure was set and controlled using an electrochemical oxygen pump and an electrochemical pO_2-sensor, respectively, made of zirconia doped with 10 mol.% yttria; the system was equipped with an automatic regulator Zirconia-M (Research technologies, Russia).

3. Results and Discussion

The $Ba_3InGa_2O_{7.5}$ sample was found to be single-phase (Figure 1). All X-ray peaks correspond to the monoclinic modification of the isostructural phases with the formula

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$A_3BGa_2O_{7.5}$ (B = REM) described in the literature [10]. Refinements of the unit cell parameters were carried out by full-profile fitting using a structureless model (the Le Bail method). The phase is characterized by monoclinic symmetry (sp. group P2/c) with the unit cell parameters a = 7.942(1) Å, b = 5.868(5) Å, c = 18.201(6) Å, β = 91.52(9).

According to the SEM images (Figure 2), the sample is characterized by a homogeneous morphology, and no phase contrast is observed. The powder consists of large particles of ~20 μm size, which are agglomerates of smaller particles of 1–5 μm size. The EDX spectrum and the content of the metal elements (an averaging over 20 points) are shown in Figure 3. The quantitative content of the metal elements in the sample agrees with the theoretical elemental composition.

Typical impedance spectra of the sample at different temperatures in dry and wet air are given in Figure 4. The spectra are represented by fragments of distorted semicircles, which include the contributions from volume (capacity values C~10^{-12}–10^{-11} F) and grain boundaries (capacity values C~10^{-10}–10^{-9} F), and an electrode process response is visible in the low frequency region.

The sum of the resistances R1 (volume) and R2 (grain boundaries) was considered as a sample resistance and used for the total conductivity calculation.

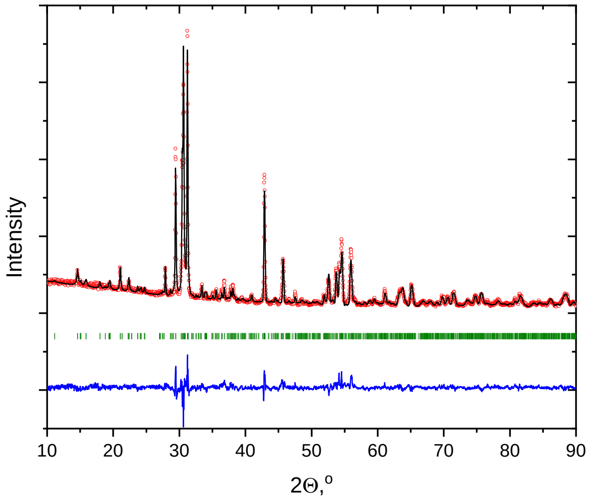

Figure 1 The XRD data. Red points are experimental, back line is calculated, blue line is difference X-ray profiles, green ticks correspond to the angular positions of the reflections.

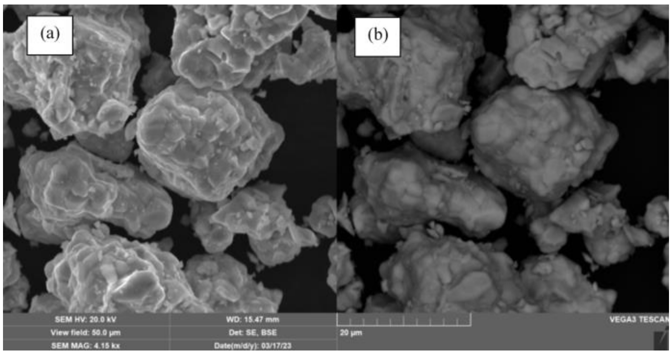

Figure 2 The SEM images of the $Ba_3InGa_2O_{7.5}$ powder, secondary electrons (SE) signal (a) and backscattered electrons (BSE) signal (b).

Temperature dependences of the total electrical conductivity in wet and dry air are given in Figure 5. The conductivity values in wet atmosphere are higher than in dry atmosphere; at 500 °C the difference in values is more than one order of magnitude. The data may be explained by the proton defects formation and, as a result, by the appearance of the proton conductivity. The water uptake for the complex oxide with incomplete oxygen sublattice may be described by the following quasichemical equation [17]:

$$V_O^{\times} + 2O_O^{\times} + H_2O = 2OH_O^{\bullet} + O_i'', \qquad (1)$$

where $V_O^{\times}$ is a structural oxygen vacancy, $O_O^{\times}$ is an oxygen ion in a regular position, $OH_O^{\bullet}$ is a proton localized on the oxygen ion, and O_i'' is an oxygen ion in a structural vacancy.

The proton conductivity appearance is also confirmed by an activation energy change. The apparent activation energy of the conductivity is 0.98 eV in dry air, which is correlated with the data for oxygen-ion transfer, and 0.51 eV in wet air, which is related to the proton transfer activation energy by the Grotthuss mechanism [18].

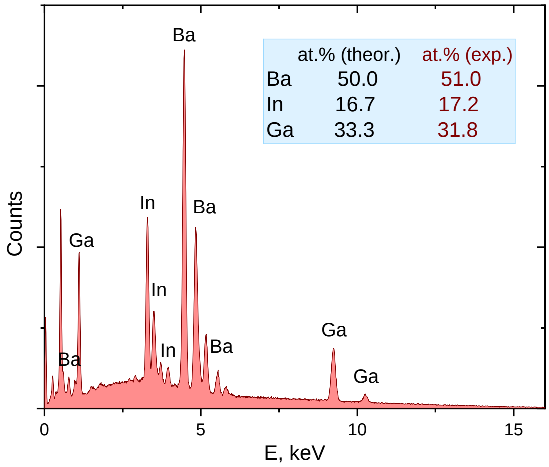

Figure 3 Qualitative analysis: the EDX spectrum and a comparison of the theoretical and experimental content of the metal elements.

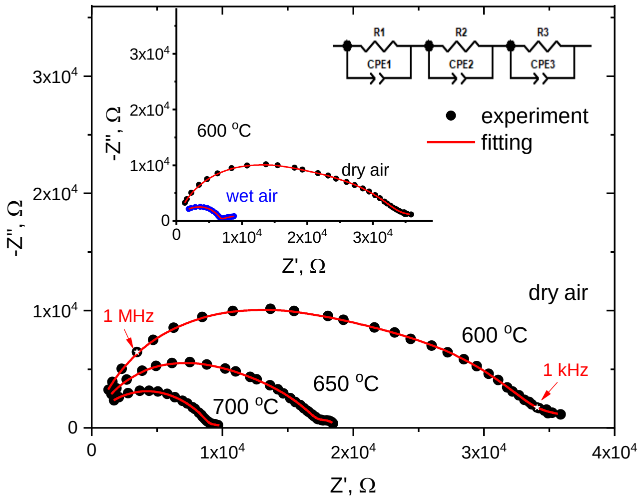

Figure 4 The typical impedance spectra and the equivalent circuit for treatment of the results: R, CPE – resistor and constant phase element of bulk (1), grain-boundary (2), and electrode (3) processes, respectively.

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A small change observed on the temperature dependence at ~570 °C in dry air is similar to those present in the conductivity dependences of the isostructural phases with the formula $Ba_3BGa_2O_{7.5}$ [11, 12] and can be associated with a possible structural transition from the high-temperature orthorhombic structure (α-phase) to the low-temperature structure with monoclinic symmetry (β-phase) [10]. But the detailed investigation of the structural transformation is a task for the future.

The electrical conductivity as a function of the oxygen partial pressure at different temperatures in dry and wet atmospheres is shown in Figure 6. The conductivity values are independent of pO_2. Considering the structural peculiarities of the sample (the presence of the structural oxygen vacancies), it can be assumed that the $Ba_3InGa_2O_{7.5}$ complex oxide is an electrolyte without electronic contribution both in dry and wet air.

The total conductivity in dry air is the oxygen-ion conductivity ($\sigma^{dry} = \sigma_{O^{2-}}$) and the total conductivity in wet air is a sum of the oxygen-ion and proton conductivities ($\sigma^{wet} = \sigma_{O^{2-}} + \sigma_{H^+}$).

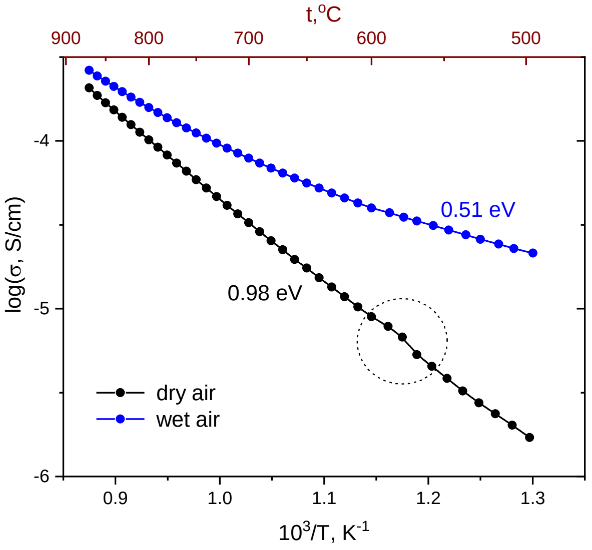

Figure 5 The temperature dependences of the total conductivity in dry and wet air.

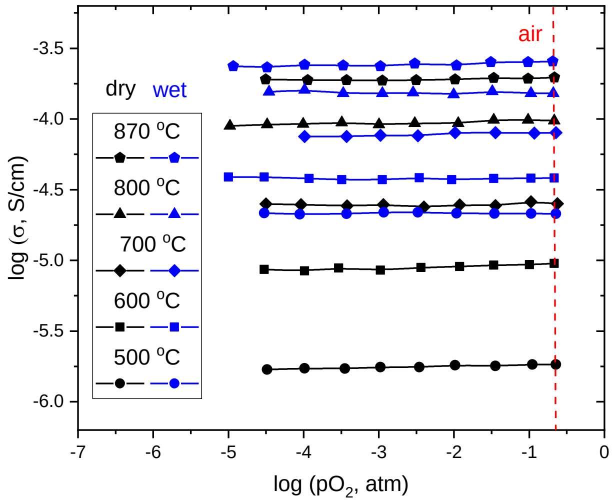

Figure 6 The total conductivity versus oxygen partial pressure in dry and wet atmospheres.

According to some studies of proton-conducting complex oxides [13, 19, 20], at high temperatures (up to 450–500 °C), where the proton concentration is low, it is possible to assume that the oxygen-ion conductivity does not significantly change in atmospheres with different pH_2O. In this case, the value of proton conductivity can be approximately estimated as the difference between the ionic conductivity values in wet and dry conditions ($\sigma_{H^+} = \sigma^{wet} - \sigma^{dry}$). The separation of the total conductivity in wet air into partial contributions (oxygen-ion and proton conductivities) and the calculated proton transport numbers ($t_{H^+} = \sigma_{H^+}/\sigma^{wet}$) vs temperature are shown in Figure 7. The $Ba_3InGa_2O_{7.5}$ complex oxide is a predominantly proton conductor at 500 °C in wet air as the proton transport number is approaching 100%.

It is interesting to compare the results with those for the isostructural complex oxides; the conductivities for some phases at 700 °C are presented in Table 1. The transport properties of the yttrium analogue with the formula $Ba_3YGa_2O_{7.5}$ were more investigated [11, 12]. The values of the conductivity obtained by several groups of researchers differ significantly, but in either case, the conductivity of the In-containing sample investigated in the present work is higher than those of the Y-containing complex oxide. This fact can be explained by the difference of the total binding strength between oxygen ions and B-elements. The In–O bond energy (90 kJ/mol) is lower than the Y–O bond energy (128 kJ/mol) (the values are calculated based on the work [21]).The decrease in the bonding energy leads to an increase in the oxygen ion mobility, as well as the mobility of protons, because the proton mobility is associated with the oxygen sublattice dynamics, which is typical of different types of complex oxides [22–24]. The minimal donor doping in A- or B-sublattice leads to the increase of the conductivity of the yttrium analogue (Table 1). So, this way of increasing the conductivity may be also promising for the $Ba_3InGa_2O_{7.5}$ complex oxide.

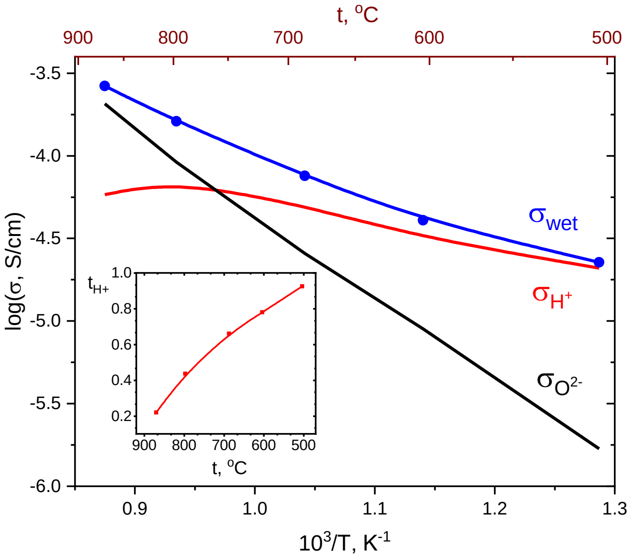

Figure 7 The temperature dependences of the total conductivity and partial (oxygen-ion and proton) conductivities in wet air. The calculated proton transport numbers versus temperature (in the inset).

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Table 1 The electrical conductivity values of the $A_3BB'_2O_{7.5}$ type complex oxides.

Complex oxide	Conductivity values at 700 °C			Ref.
	σ_{dry}, S/cm	**σ_{wet}, S/cm**	**σ_{H+}, S/cm**	
$Ba_3InGa_2O_{7.5}$	$3.4\cdot10^{-5}$ (air)	$7.9\cdot10^{-5}$ (air)	$4.5\cdot10^{-5}$	[present work]
$Ba_3YGa_2O_{7.5}$	$1.7\cdot10^{-6}$ (air)	$5.2\cdot10^{-6}$ (air)	$3.5\cdot10^{-6}$	[13]
	$9.1\cdot10^{-6}$ (N_2)	$3.5\cdot10^{-5}$ (N_2)	$2.6\cdot10^{-5\,a}$	[12]
	–	$3.5\cdot10^{-5}$ (air)^b	–	[12]
$BaSr_2YGa_2O_{7.5}$	$1.1\cdot10^{-6}$ (N_2)	$2.5\cdot10^{-6}$ (air)^b	–	[11]
$Sr_3YGa_2O_{7.5}$	$9.5\cdot10^{-7}$ (N_2)	$1.9\cdot10^{-6}$ (air)^b	–	[11]
$Ba_{2.9}La_{0.1}YGa_2O_{7.55}$	$1.7\cdot10^{-4}$ (N_2)	$3.4\cdot10^{-4}$ (air)^b	–	[12]

[a] The value calculated from the results in dry and wet N_2;
[b] The measurements were done in air without control of pH_2O (mostly wet).

The $Ba_3InGa_2O_{7.5}$ complex oxide was found to demonstrate the proton conductivity in wet air, but the phase is chemically stable under high water vapor pressure only at the temperatures above 450–500 °C. The sample may reversibly intercalate only small amount of water molecules. The water uptake at ~500 °C is not more than 0.05 mol H_2O per formula unit (see Supplementary materials). The dissociative process of water uptake for the high-temperature range does not lead to chemical destruction and can be described using the quasichemical method (Equation 1). But the further intercalation of H_2O into the complex oxide structure at lower temperatures leads to a chemical interaction of the substance with water molecules.

The complex investigation (X-ray diffraction, electron microscopy, thermogravimetry) of the $Ba_3InGa_2O_{7.5}$ sample after the treatment at 250 °C in the atmosphere with high pH_2O (see Supplementary materials) demonstrates the hydrolysis decomposition of the phase according to the chemical reaction:

$$\begin{gathered}Ba_3InGa_2O_{7.5} + (2+x)H_2O = Ba(OH)_2\cdot xH_2O + \\ BaGa_2O_4 + 0.5Ba_2In_2O_4(OH)_2.\end{gathered} \tag{2}$$

In the work [12], a similar behavior was found for the $Ba_3YGa_2O_{7.5}$ complex oxide, for it also hydrolysed during the prolonged treatment in wet atmosphere. Doped samples based on the $Ba_3YGa_2O_{7.5}$ phase were not investigated at low temperatures in wet air, so their possible hydrolysis decomposition is not discussed [11, 12].

4. Limitations

The main problem of the investigated complex oxide is its full hydrolysis in water vapors. On the one hand, we may assume that this is a common feature of the structural type of the $A_3BB'_2O_{7.5}$ (A = alkaline-earth metal, B = REM, In^{3+}; B' = Ga^{3+}, Al^{3+}) compounds. The condensation polyhedra $[B'_2O_7]$ in the structure may transform to the isolated polyhedra during their interaction with water molecules $[B'_2O_7] + H_2O = 2[B'O_3(OH)]$, leading to significant changes in the structure and to the subsequent destruction. On the other hand, a chemical nature of the B/B' cations may also determine the process. The Al-containing phases may be more resistant to hydrolysis decomposition as compared with the Ga-containing phases, and partial substitution of In^{3+} positions with Al^{3+} may also lead to the water uptake decrease by analogy with solid solutions $Ba_2In_{2-x}Al_xO_5$ [25]. These assumptions require further studies.

5. Conclusions

The $Ba_3InGa_2O_{7.5}$ complex oxide is an oxygen-ion conductor in dry air and a predominantly proton conductor in wet air at temperatures below 700 °C. The conductivity values are on the average level (the total conductivity is $7.9\cdot10^{-5}$ S/cm at 700 °C and $pH_2O = 2\cdot10^{-2}$ atm), but these values are higher than those for the $Ba_3YGa_2O_{7.5}$ compound described in the literature. The $Ba_3InGa_2O_{7.5}$ phase is chemically unstable during the treatment in atmosphere with high water vapor pressure at temperatures lower 450 °C, so it is difficult to consider the investigated complex oxide as a proton electrolyte for the practical uses. However, the complex oxide can be proposed as a base compound for obtaining of the solid solutions with substitution of A- or B-sublattice by different type of dopants, which may both increase the stability to the hydrolysis decomposition and improve the electrical properties.

• Supplementary materials

This manuscript contains supplementary materials, which are available on a corresponding online page.

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Supervision: N.K.
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Visualization: N.K., V.Ch., A.G.
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Writing – review & editing: N.K., V.Ch.

• Conflict of interest

The authors declare no conflict of interest.

• Additional information

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