Transport properties of ceramic composites based on bismuth and indium oxides

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Abstract. Solid solutions based on indium oxide In2–xZrxO3+0.5x (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.05, 0.075, 0.1) were synthesized and temperature dependences of their conductivity at 25-800 °C were investigated. It was found that In1.985Zr0.015O3.0075 solid solution possessed the highest conductivity of about 10⁰ S/cm at 800 °C.

Dense In1.985Zr0.015O3.0075–50 vol.% Bi2O3 ceramic composite was obtained and investigated, its microstructure was studied, and the formation of fine-grained structure with homogeneous distribution of components by volume was demonstrated. The total conductivity of composite was measured, and oxygen fluxes for composite 1.7 mm thick membrane at 750-800 °C was obtained. The oxygen flux was found to be 2.4 × 10⁻⁷ mol·cm⁻²·s⁻¹ at 800 °C when oxygen partial pressures on both sides of membrane was 0.21 atm/0.017 atm, while the oxygen selectivity was more than 20. This indicates the promising of investigated composite to use as an intermediate-temperature (750-800 °C) ion transport membrane for obtaining of pure oxygen from air.

1. Introduction

Nowadays the membrane technologies are actively used to produce oxygen of high purity from air and other oxygen-containing gas mixtures [1-2]. The process of separation the air components can be carried out using dense ceramic ion transport membranes (ITM) capable of selectively passing of pure oxygen under given temperatures (> 700 °C) being by the gradient of its partial pressures. However, many of known ceramic ITM fabricated by single-phase multicomponent oxides (e.g. by BSCF or LSCF) with high mixed oxygen-ion and electronic conductivity may degrade during long-term operation due to their insufficient chemical or thermal stability [3-4], while their oxygen transport productivity of work is lowering. The solution of this problem is the creation of more stable composite membranes for long-term use, in which one of the components is electronic conductor and the other is an oxygen-ionic conductor. For example, ceramic composites based on In2O3 – Bi2O3, in which indium oxide (an electron conductor) is chemically and thermally compatible with bismuth oxide having high oxygen-ionic conductivity, have been proposed and investigated earlier [5-7]. For further application of these composites as materials of ion transport membranes, their electronic conductivity needs to be increased, which is possible by replacing pure In2O3 with solid solutions based on it. As it is known from the literature when doping of In2O3 by oxides of tetravalent cations (for example, by SnO2), the electronic conductivity can be increased by several orders of magnitude [8-9], what is currently principally used in microelectronics to create conductive coatings, LEDs, sensors, etc.
The main goals of this work are synthesis and study the conductivity of In$_2$Zr$_x$O$_{3+0.5x}$ (x = 0.005-0.1) solid solutions, the detection of optimum zirconia additive when maximum for their conductivity is achieved; as well as obtaining and investigating the transport properties of ceramic composites "indium oxide doped with zirconia" - "bismuth oxide" to create new oxygen-permeable ITM materials.

2. Experimental
Solid solutions of In$_2$Zr$_x$O$_{3+0.5x}$ (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.05, 0.075, 0.1) were obtained from indium (III) and zirconium (IV) oxides (99.999 % of purity), which were taken in the required proportions. The charges for synthesis of solid solutions were mixed in a planetary mill Pulverisette 5 at a speed of 200 rpm with addition of ethyl alcohol in a ratio of 1:1 to the total weight of samples. Homogenization of powder mixtures was carried out for 30 min by using of agate bowls and balls (mass ratio of charges to balls was 1 to 10). Next the charges were held in a drying oven for 5 hours at 120 °C to remove alcohol and moisture, then were cold pressed at 200 MPa into parallelepipeds (a = 5 mm, b = 5 mm, l = 40 mm) with addition of a binder – 5 % aqueous solution of polyvinyl alcohol (5 % to the total mass of charges). The obtained green bodies were held in a drying oven for 5 hours at 200 °C to remove moisture, then were placed in a muffle furnace and calcined on platinum substrates in air atmosphere at 1200 °C for 100 hours, the heating and cooling rate of the furnace was 2 °C/min.

To synthesize a ceramic composite of In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ – 50 vol.% Bi$_2$O$_3$, the sintered samples of In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ were ground in an agate bowl to the powder size of 2-3 μm. This powder then was mixed with 50 vol.% Bi$_2$O$_3$ (99.999 % of purity), taking the densities of In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ and Bi$_2$O$_3$ equal to 7.15 g/cm$^3$ and 8.9 g/cm$^3$, respectively. The powder mixture was cold pressed at 200 MPa into tablets (Ø = 30 mm, h = 2.5 mm and Ø = 6 mm, h = 3 mm) for measuring the oxygen fluxes, porosity and linear thermal expansion, and into parallelepipeds (a = 5 mm, b = 5 mm, l = 40 mm) for measuring of the conductivity. Next the samples were held for 5 hours at 200 °C in a drying oven, and then were calcined at 800 °C for 10 hours on platinum substrates in a muffle furnace; the heating and cooling rate of the furnace was 2 °C/min. The shrinkage of all samples during sintering was about 20 %.

X-ray phase analysis of both In$_2$Zr$_x$O$_{3+0.5x}$ (x = 0.005-0.1) solid solutions and In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ – 50 vol.% Bi$_2$O$_3$ ceramic composite was investigated by Shimadzu XRD-6000 diffractometer (CuKα -radiation, 20 range of 10 - 70°, step for scan of 0.1°). The decoding of X-ray diffraction patterns was performed using ICDD PDF-2 database. Microstructure of polished cross section for the composite, which had been prepared by STRUERS equipment, was investigated by Olympus GX-51 optical microscope. Open, closed and total porosity of the composite was measured by hydrostatic weighing.

The conductivity of both In$_2$Zr$_x$O$_{3+0.5x}$ (x = 0.005-0.1) solid solutions and In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ – 50 vol.% Bi$_2$O$_3$ ceramic composite was measured by four-probe method in ambient air in potentiostatic mode (0.1 V) at 20-800 °C. The measurements were carried out on a Solartron 1285A potentiostate in steps of 50 °C and holding for 30 min at each temperature point to reach a steady state.

The measurements of oxygen fluxes for In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ – 50 vol.% Bi$_2$O$_3$ composite (tablet of Ø = 25 mm, h = 1.7 mm) were performed by gas chromatography technique at 750 °C, 775 °C, 800 °C on Crystallux-4000M gas chromatograph. To do this, the polished tablet was tightly connected to the end of the measuring cell, which was placed into a tube furnace and heated to the temperature of 750-800 °C. From the outside face, the tablet was in contact with air, and from the inner face it was connected to a gas chromatograph, while the sweep gas (helium) was blown through the measuring cell to remove the gas mixture penetrated through the sample. The selectivity of composite membrane was evaluated by the ratio of concentrations of oxygen over nitrogen in the analyzing gas mixture (consisted of oxygen, nitrogen, and helium). The rate of sweep gas flow was 5-20 ml/min.

The linear thermal expansion of the In$_{1.985}$Zr$_{0.015}$O$_{3.0075}$ – 50 vol.% Bi$_2$O$_3$ composite was measured under argon atmosphere on DIL 402 C dilatometer in a Netzsch tube furnace at 20-800 °C. Composite (tablet of Ø = 5 mm, h = 2.5 mm) was placed in a holder with high-precision displacement converter. The rate of argon flow was 70 ml/min, the rate of heating and cooling of the furnace was 10 °C/min.
3. Results and discussion
X-ray phase analysis of In$_{2-x}$Zr$_x$O$_{3+0.5x}$ (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.05, 0.075, 0.1) solid solutions indicates that In$_2$O$_3$ with bixbyite crystal structure (JCPDS No. 71-2194, Ia3 space group) is the main phase, and its lattice parameter a = 10.119 Å does not vary in all samples within the error of ± 0.005 Å). The presence of insignificant traces of second phase - ZrO$_2$ of tetragonal modification (JCPDS No. 81-1544, P42/mmc space group) is also detected in In$_{2-x}$Zr$_x$O$_{3+0.5x}$ (x = 0.025, 0.05, 0.075, 0.1) samples. Thus, it can be concluded that the solubility limit of zirconia in In$_2$O$_3$ bixbyite is in the range of 0 < x < 0.025. This is confirmed by temperature dependences of total electrical conductivity for In$_{2-x}$Zr$_x$O$_{3+0.5x}$ (x = 0.005-0.1) solid solutions, which are presented in Figure 1a. The conductivity of all samples increases at an increase in the temperature in both ranges of 20 - 300 °C and 500 - 800 °C, but, on the contrary, decreases in the range of 300 - 500 °C. This is due to the features of temperature dependence of conductivity for the impurity semiconductor. At a low temperature of 20-300 °C, the concentration of free charge carriers on donor sublevel rises at an increase in the temperature, resulting to increase in total conductivity. At the second temperature range of 300 - 500 °C, an impurity donor sublevel becomes depleted, while the charge carriers pass into the conduction band, resulting to metallic conductivity. When increasing the temperature to the range of 500-800 °C, the intrinsic conductivity of the semiconductor becomes activate, so the total conductivity of all samples increases. The maximum of conductivity as for room temperature of 20 °C as for 800 °C is detected for In$_{1.985}$Zr$_{0.015}$O$_{3+0.0075}$ solid solution (Figure 1b), so it can be concluded that solubility limit of zirconia in In$_2$O$_3$ bixbyite is reached at x = 0.015. The conductivity of In$_{1.985}$Zr$_{0.015}$O$_{3+0.0075}$ solid solution at 800 °C is almost two orders of magnitude higher than that for pure In$_2$O$_3$, therefore this solid solution was chosen for preparing the composite with Bi$_2$O$_3$.

![Figure 1a. Temperature dependences of the conductivity (σ) of In$_{2-x}$Zr$_x$O$_{3+0.5x}$ (x = 0, 0.005, 0.01, 0.015, 0.02, 0.025, 0.05, 0.075, 0.1)](image)

![Figure 1b. Zirconia dopant concentration (x) dependences of the conductivity (σ) of In$_{2-x}$Zr$_x$O$_{3+0.5x}$ (x = 0-0.1) at 20 °C and at 800 °C)](image)

Figure 2a illustrates the micrograph of polished section of In$_{1.985}$Zr$_{0.015}$O$_{3+0.0075}$ - 50 vol.% Bi$_2$O$_3$ composite prepared by sintering at 800 °C in ambient air atmosphere for 10 hours. Ceramic composite with fine-grained structure is formed, where the dark and the light components (In$_{1.985}$Zr$_{0.015}$O$_{3+0.0075}$ and γ-Bi$_2$O$_3$, respectively, as it has been confirmed by X-ray phase analysis data) are evenly distributed. Total porosity of the ceramic composite is about 3 %, while its open porosity is of 0.15 %, which indicates the formation of high-density material by sintering. It is notable that X-ray diffraction pattern of the composite contains no peaks belonging to α-Bi$_2$O$_3$, since in the binary In$_2$O$_3$ - Bi$_2$O$_3$ system the metastable δ-Bi$_2$O$_3$ → γ-Bi$_2$O$_3$ transformation is realized upon cooling of the material after sintering. According to the known literature data [10], this is because γ-Bi$_2$O$_3$ syenite (space group I23, lattice parameter a = 10.264 Å) crystal structure is relevantly close to In$_2$O$_3$ bixbyite (space group Ia3, lattice parameter a = 10.119 Å). From this point of view, the presence of metastable state in this system, due to exhibiting of Dankov-Konobeevsky effect of the orientation-dimensional structural accordance, is
favorable for further application of this composite as the material of ion transport membrane. So, this composite is allowed to be mechanically stable and free from cracks formation during thermal cycling. As it is known ceramics based on pure bismuth oxide has low mechanical stability due to dramatic polymorphous transformation of \( \alpha \)-Bi\(_2\)O\(_3\) \( \rightarrow \) \( \delta \)-Bi\(_2\)O\(_3\) leading to a significant change in volume (6-8 \%), which is accompanied by cracking [11]. Indeed, in this composite material this mechanical drawback has been overcome, that is confirmed by dilatometric studying of its linear thermal expansion, where the length change of the sample at \( \gamma \)-Bi\(_2\)O\(_3\) \( \rightarrow \) \( \delta \)-Bi\(_2\)O\(_3\) polymorphic transformation at 670-700 °C is less than 0.5 \% (Figure 2b). This polymorphous transformation has been found to be reversible, while the linear thermal expansion coefficient for In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) – 50 vol.% Bi\(_2\)O\(_3\) composite is observed to be \( 3.2 \times 10^{-5} \) K\(^{-1}\) at the temperature range of 400-670 °C.

Figure 2a. Microstructure of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) – 50 vol.% Bi\(_2\)O\(_3\) composite, calcined at 800 °C during 10 hours

Figure 2b. Temperature dependences for linear thermal expansion (\( \Delta l/l \)) of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) – 50 vol.% Bi\(_2\)O\(_3\) composite

Figure 3a. Temperature dependences of the conductivity (\( \sigma \)) of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) – 50 vol.% Bi\(_2\)O\(_3\) composite, of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) solid solution, of pure In\(_2\)O\(_3\), and of pure Bi\(_2\)O\(_3\).

Figure 3b. Dependences of the oxygen flux (\( j \)) of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) – 50 vol.% Bi\(_2\)O\(_3\) composite 1.7 mm thick membrane on its partial pressure difference (log \( P_{\text{out}}/P_{\text{in}} \)) at 750-800 °C

Figure 3a shows the temperature dependences for the conductivity of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) – 50 vol.% Bi\(_2\)O\(_3\) composite, of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) solid solution, of pure In\(_2\)O\(_3\), and of pure Bi\(_2\)O\(_3\). Up to 800 °C, the conductivity of composite varies insignificantly. Maximum of conductivity for the composite reaches the value of 8 S/cm at 800 °C, which exceeds the conductivity of pure \( \delta \)-Bi\(_2\)O\(_3\) and In\(_2\)O\(_3\) at this temperature. Consequently, it is because of the presence of a percolated net of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) solid solution in the composite (the conductivity of In\(_{1.985}\)Zr\(_{0.015}\)O\(_{3.0075}\) solid solution is about 100 S/cm at 800 °C), which is also confirmed by its microstructure (Figure 2a). Figure 3b presents the oxygen fluxes for the 1.7 mm thick composite membrane at 750 °C, 775 °C and 800 °C. As it can be seen the
oxygen flux increases at an increase in both the temperature and the partial pressure of oxygen on the outer/inner sides of the membrane, which responds to Wagner's theory of oxygen transfer in diffusion regime [12]. The maximum of oxygen flux at a difference of its partial pressures 0.21 atm/0.017 atm on both sides of membrane reaches a value of $2.4 \times 10^{-7}$ mol∙cm$^{-2}$∙s$^{-1}$ at 800 °C, while the selectivity of membrane (the flux of oxygen vs the flux of nitrogen) has been more than 20, which indicates the promise of using this composite material as an ion transport membrane to produce of pure oxygen from air. It should also be noted that this membrane material is allowed to be chemically stable during long-term operation in the presence of "acidic" (i.e., CO$_2$ and SO$_2$) gases in ambient air atmosphere, because indium and bismuth oxides are tolerant to them. As it is known this condition are not completely withstand by BSCF membranes [3-4], containing of alkaline earth barium and strontium. A further increase in the selectivity of membrane can be reached by lowering the total porosity of material, which may be achieved by controlling the particle size distribution of the initial powder charge together with applying hot pressing for consolidation of the green bodies.

4. Conclusions
A new membrane material has been synthesized that has a great potential to use in the tasks for concentrating of pure oxygen from air. The main disadvantage of this material is permanently increasing the cost of indium oxide, which is an order of magnitude higher than the cost of bismuth oxide. Apparently, a further subject of research will be the replacement of solid solutions based on indium oxide to cheaper oxides with comparable electronic conductivity, but also well compatible to bismuth oxide having an outstanding ionic conductivity.

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