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Conference Paper

The Effect of Simultaneous Homo- and Heterogeneous Doping on Transport Properties of $Ba_2In_2O_5$

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Abstract

In this article, the possibility of application of simultaneous homogeneous and heterogeneous doping has been described for the first time. The composite $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6$ has been obtained by *in situ* solid-state method. The scanning electron microscopy and thermogravimetry investigations have been carried out; the electrical properties have been examined. It has been proved that simultaneous homogeneous and heterogeneous doping is a prospective method for obtaining high-conductive proton electrolytes.

Keywords: brownmillerite, composite, anionic doping, fluorine

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1. Introduction

One of the key positions of modern materials science is the research and development of solid oxide fuel cells and their components, including electrolytic membrane materials. It is necessary to find inexpensive and technological solid electrolyte with high conductivity and stability at high temperature, in oxidizing and reducing atmosphere. Medium temperatures are the most optimal region in terms of energy costs. Prospective ionic conductors for this temperature range are proton electrolytes based on the complex oxides.

The most studied method for modification of their structure and optimization of physicochemical properties is a homogeneous cationic doping [1–5]. However, the homogeneous anionic doping is a new promising way for the obtaining of new materials with improved properties. Earlier, we have reported a new route for increasing oxygen-ion and proton conductivities by F^--doping of brownmillerite $Ba_2In_2O_5$ [6]. It has been proved that small F^--concentrations can improve the oxide-ion (mixed anion

effect) and the proton conductivities. The other prospective method of improving transport properties is a heterogeneous doping. The composites based on $Ba_2In_2O_5$ with chemically inert Ba_2InNbO_6 oxide phase as a heterogeneous dopant demonstrate significant increase of conductivity level. The maximum conductivity corresponds to the ratio of the components 0.7:0.3 [7]. In this work the possibility of application of simultaneous homogeneous and heterogeneous doping has been described for the first time. The composite $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6$ has been chosen for the investigation.

2. Methods

We used *in situ* solid-state method for preparing the composite. This method consisted in simultaneous synthesis of the components from starting materials in the same reaction mixture:

$$1.93BaCO_3 + 0.85In_2O_3 + 0.15Nb_2O_5 + 0.035BaF_2 \xrightarrow{t}$$

$$0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6 + 1.93CO_2$$

(1)
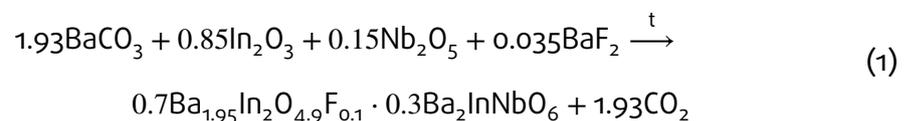
using temperature treatments 800–1300°C, six stage 24h each.

The X-ray powder diffraction (XRD) measurements were made on a Bruker Advance D8 diffractometer with Cu K$_\alpha$ radiation. The crystal structure of the sample was determined through Rietveld refinement using FULLPROF software.

The surface morphology and local chemical composition were studied using a workstation AURIGA CrossBeam (Carl Zeiss NTS) and JEOL JSM 6390 LA scanning electron microscope with console JEOL JED-2300. The detection limit at ordinary energies (5–20 kV) was ∼ 0.5 at.%; the concentration measurement error was ± 2%.

Thermogravimetric analysis was carried out on 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 (pH_2O = 2·10^{-2} atm). The cooling was performed 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 ceramics used for the electrical measurements were prepared by pressing disk-shaped samples at 250–300 MPa and sintering them at 1300°C for 24h 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 3h. The *ac* conductivity of the samples (2-probe method) was measured using a Z-1000P (Elins) impedance spectrometer within the frequency range of $1-10^6$ Hz. The conductivity measurements were carried out under dry and wet air varying the temperature and partial oxygen pressure pO_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 the saturated solution of KBr ($pH_2O = 2 \cdot 10^{-2}$ atm). The 'dry' air was produced by flowing the gas through P_2O_5 ($pH_2O = 3.5 \cdot 10^{-5}$ atm). The humidity of gases was measured by H_2O-sensor ('Honeywell' HIH-3610).

3. Results

According to XRD analysis, the sample contained two phases – cubic perovskite type Ba_2InNbO_6 phase (*Pm3m* space group) and brownmillerite type $Ba_{1.95}In_2O_{4.9}F_{0.1}$ phase (*I4cm* space group) with partial disordering of oxygen vacancies. The lattice parameters were $a = 4.142$ Å for Ba_2InNbO_6 and $a = 5.950(2)$ Å, $c = 16.813(9)$ Å for $Ba_{1.95}In_2O_{4.9}F_{0.1}$. They were in a good agreement with previously reported data [7]. XRD-pattern for $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6$ refined by Rietveld analysis is presented in Figure 1.
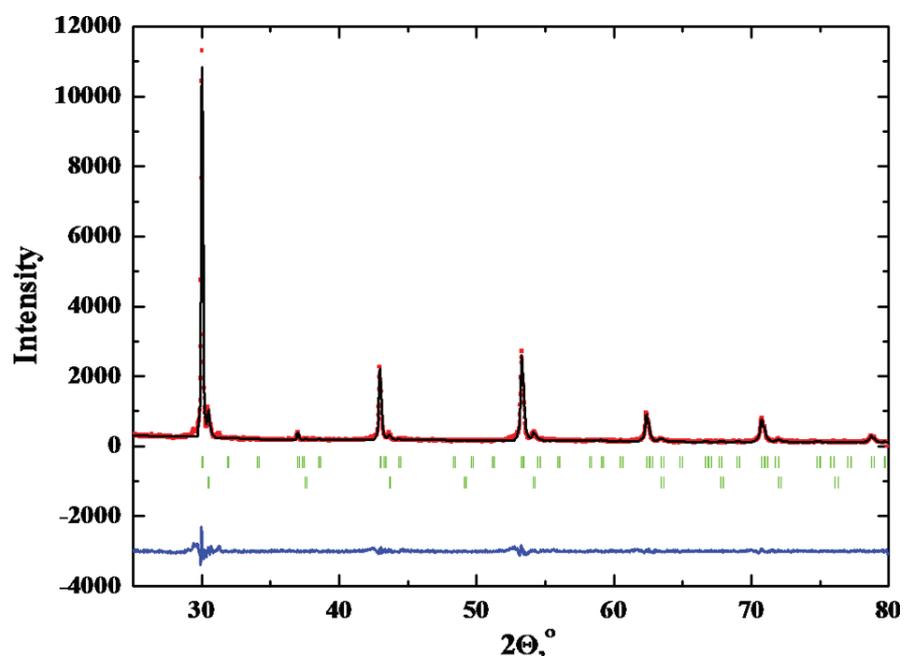
Figure 1: XRD patterns of $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6$. At the bottom of the figure – the difference between the experimental data and the calculated ones after refinement. Vertical bars show the Bragg angle positions.

The morphology of the samples was studied by scanning electron microscopy (SEM) (Figure 2). It can be seen for individual phases $Ba_{1.95}In_2O_{4.9}F_{0.1}$ (Figure 2(a)) and Ba_2InNbO_6 (Figure 2(b)) and for composite system (Figure 2(c)) that the grain size was approximately 5–10 µm and the grain boundaries were clean. The microelement analysis showed the presence of all main elements in the samples.
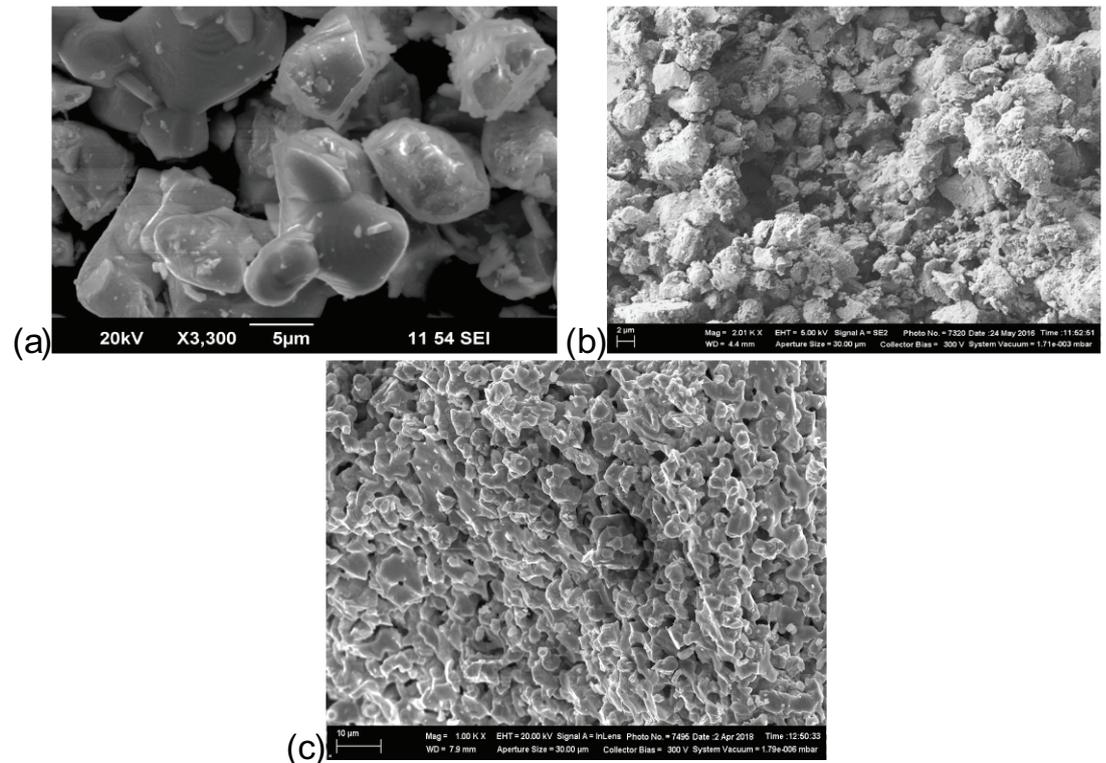
Figure 2: SEM image of individual phases $Ba_{1.95}In_2O_{4.9}F_{0.1}$(a), Ba_2InNbO_6 (b), and composite system $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6$ (c).

Thermal analysis of the composite system showed that the composite changed mass at temperatures 300–500°C in wet atmosphere ($pH_2O = 2 \cdot 10^{-2}$atm), which corresponded to the processes of removing water molecules (Figure 3). The maximal water uptake for composite system is proportional to the content of the phase $Ba_{1.95}In_2O_{4.9}F_{0.1}$ with incompletion in the oxygen sublattice and is 0.60 mole H_2O per formula $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3 Ba_2InNbO_6$. The Ba_2InNbO_6 phase is nominally complete in the oxygen sublattice and is capable of absorbing only small amounts of water due to an insignificant change in stoichiometry during the synthesis. Thus, the main amounts of proton defects are concentrated in the grains of the phase $Ba_{1.95}In_2O_{4.9}F_{0.1}$.

The conductivity measurements were carried out under dry ($pH_2O = 3.5 \cdot 10^{-5}$ atm) and wet ($pH_2O = 2 \cdot 10^{-2}$ atm) air by varying the temperature (250–1000°C) (Figure 4). The conductivity values of composite system $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3 Ba_2InNbO_6$ are significantly higher than those for both undoped $Ba_2In_2O_5$ composition and F-doped
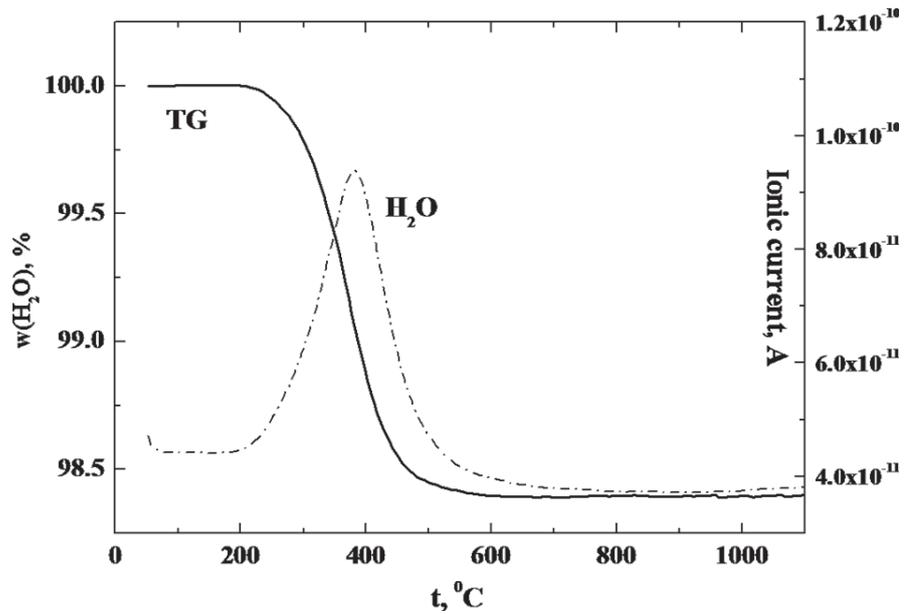
Figure 3: Thermogravimetry and mass-spectra data for hydrated sample $0.7Ba_{1.95}In_2O_{4.9}F_{0.1}\cdot0.3Ba_2InNbO_6$.

$Ba_{1.95}In_2O_{4.9}F_{0.1}$ one in the whole temperature range. The increasing in conductivity under wet air for the composite proves the ability of the sample to the proton transfer.
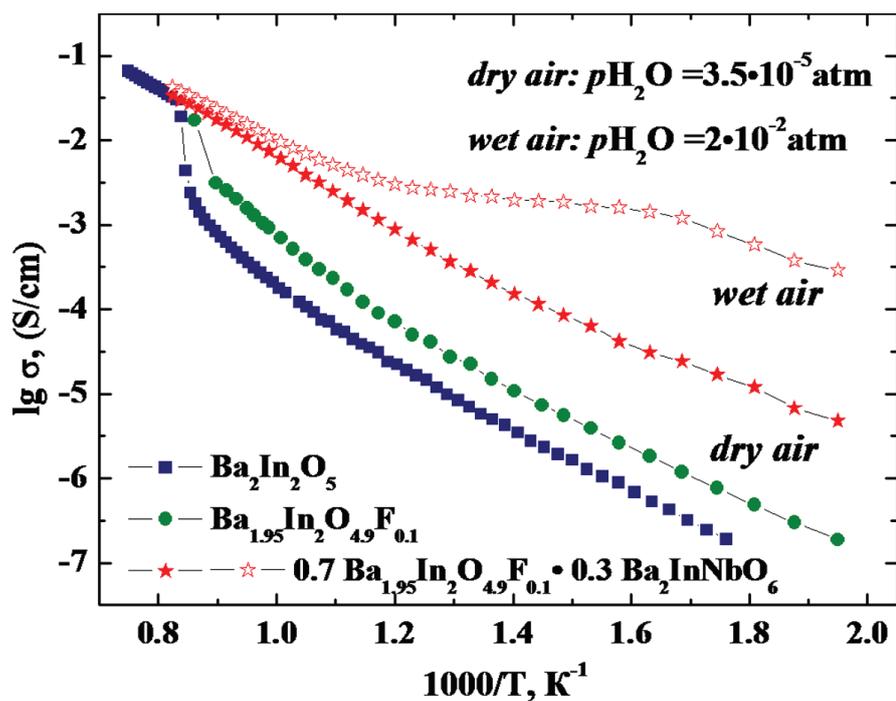
Figure 4: Electric conductivity of $Ba_2In_2O_5$ [6], $Ba_{1.95}In_2O_{4.9}F_{0.1}$ [6] and composite system $0.7Ba_{1.95}In_2O_{4.9}F_{0.1}\cdot0.3Ba_2InNbO_6$.

4. Conclusion

In this article, the possibility of application of simultaneous homogeneous and heterogeneous doping has been described for the first time. The composite $0.7Ba_{1.95}In_2O_{4.9}F_{0.1} \cdot 0.3Ba_2InNbO_6$ has been obtained by *in situ* solid-state method. It has been proved that composite sample is capable for water uptake and for proton transfer. The increasing in the conductivity values for the composite sample comparing with conductivity for the individual phases allows concluding that simultaneous homogeneous and heterogeneous doping is prospective method for obtaining high-conductive proton electrolytes.

Funding

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