

BIMEVOX materials for application in SOFCs

J. CHMIELOWIEC^{*}, G. PAŚCIAK, P. BUJŁO

Electrotechnical Institute Division of Electrotechnology and Materials Science,
M. Curie-Skłodowskiej 55/61, 50-369 Wrocław, Poland

Presented work concerns BIMEVOX (bismuth metal vanadium oxide) based solid electrolytes doped with rare earth elements (lanthanum). Investigations of melting point and compositions of elaborated materials were performed with the DTA and X-ray measurements. For determination of conductivities, the impedance spectroscopy method was applied. The influence of the material composition ($\text{Bi}_4\text{V}_2\text{O}_{11}$ doped with La), sintering time and gas atmosphere (air, reducing) on the conductivity was examined.

Key words: *fuel cell; solid electrolyte; BIVOX; SOFC*

1. Introduction

The element of a solid oxide fuel cell (SOFC) having the greatest impact on the fuel cell efficiency, production costs and stable operation, is the electrolyte. The most suitable electrolyte should possess high ionic conductivity (at minimum 0.01 S/cm) at relatively low temperature, impermeability for gases, good resistance to thermal shocks as well as good thermodynamic stability, especially in reducing atmosphere.

Nowadays, stabilized ZrO_2 (zirconium oxide) is the most often used and known type of the electrolyte for SOFC [1]. This material has suitable electrical parameters and mechanical strength but its main disadvantage is very high working temperature (800–1000 °C) limiting commercial application of this material. A real challenge for scientists is to develop new materials with high conductivities (comparable to ZrO_2) and operating below 600 °C. Suitable candidates seem to be doped Bi_2O_3 or CeO_2 but those materials exhibit increase of departure from stoichiometric composition in oxygen sublattice at low oxygen pressure. As a result, in CeO_2 based electrolytes the unwanted component of electronic conductivity appears and in the case of Bi_2O_3 based electrolytes this yields to decomposition to metallic bismuth [3–5]. Both electrolytes are the subject of research in order to obtain the materials with properties which enable application in fuel cells. Numerous papers have been published on the properties

^{*}Corresponding author, e-mail: chmielowiec@iel.wroc.pl

of $\text{Bi}_4\text{V}_2\text{O}_{11}$ doped with Cu, Co, Y, Mg, Ti, Zr, Sc [6–11]. Products synthesized in this way belong to BIMEVOX family with stabilized high temperature γ -phase of $\text{Bi}_4\text{V}_2\text{O}_{11}$. The goal of research presented in the paper are investigations of BIMEVOX doped with lanthanum and determination if La dopant influences the phase composition and conductivity of this material.

2. Experimental

The electrolyte materials $\text{Bi}_4\text{V}_2\text{O}_{11}$ (molar fraction of Bi_2O_3 – 68.5%) and those doped with La (mass fraction of La – 1, 2, 3, 6, 8 and 10%) were fabricated by solid-state reaction from stoichiometric amounts of chemically pure oxides: Bi_2O_3 (Aldrich 99.9%), V_2O_5 (Riedel de Hahn 99.5%) and La_2O_3 (Aldrich 99.9%). The initial composition was mixed and milled in a ball mill for 24 h in dry condition. Obtained mixture was dried at 400 °C for 1 h to completely remove remaining humidity and break up any large agglomerates. The electrolyte samples had form of tablets which were pressed at room temperature under 600 kG/cm². Next multi step sintering process took place and the samples were sintered for 1, 5 and 10 h at temperatures below melting point of the materials. The melting points were determined by the differential thermal analysis (DTA) [12]. The compositions were characterized by X-ray powder diffraction (Siemens D5000 goniometer).

Conductivities were determined by the impedance spectroscopy method at a wide frequency range (20 Hz–1 MHz) with the HP 4284A LCR meter, 20 mV_{rms} test signal was applied [13, 14]. Measurements were taken on round shaped samples (1.3 mm thick) in air and pure nitrogen atmosphere ($\text{O}_2 \leq 30$ ppm) as well as in vacuum (10^{-3} Tr). Conductivity measurements were also performed during a short test (2 h/650 °C) in pure reducing atmosphere. Propane–butane was used as a reducing gas. The platinum current electrodes were applied directly on the sample.

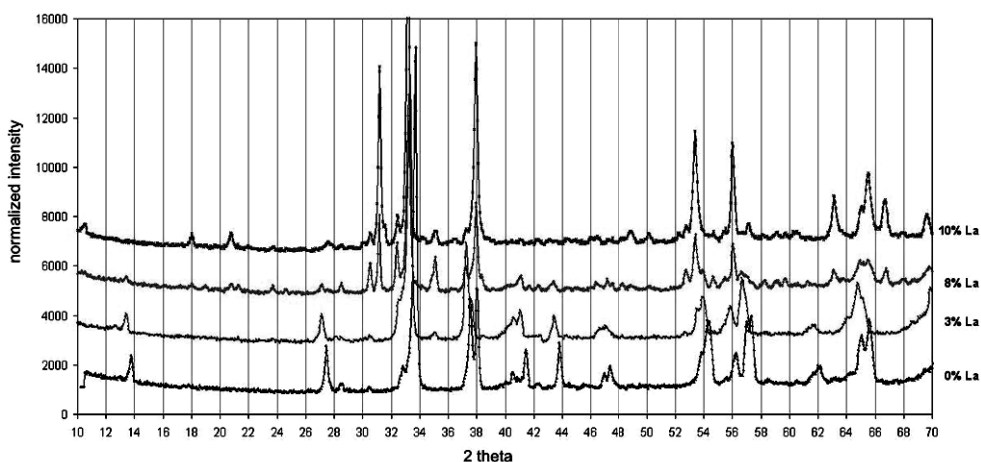
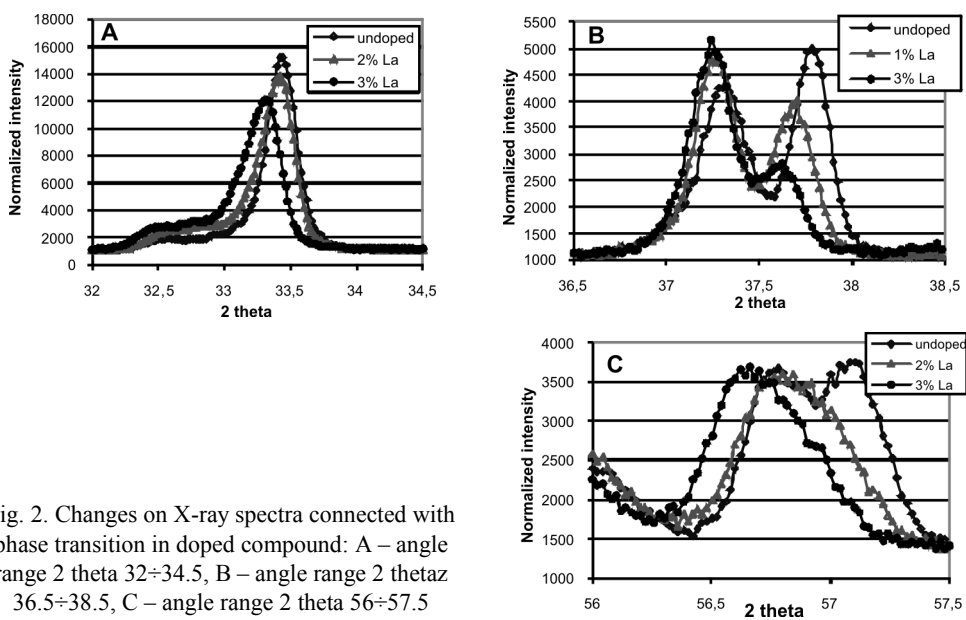
3. Results and discussion

Melting points of synthesised compositions are listed in Table 1. It was observed that the greater content of La dopant is, the higher melting point is measured. The results of X-ray measurements show significant influence of La addition (0–10%) on the phase composition of samples (Fig. 1). The X-ray spectra recorded for undoped samples and for those doped up to 3% are very similar.

Differences seen after detailed analysis (Fig. 2) are probably caused by a phase change $\alpha \rightarrow \gamma$ which occurs for polymorphic modification $\text{Bi}_4\text{V}_2\text{O}_{11}$. In Figure 2A (angle range 32–34.5°), the shift of the maximal reflection of $\text{Bi}_4\text{V}_2\text{O}_{11}$ phase is shown towards smaller 2θ angles together with increasing amount of dopant. Figure 2B presents disappearing of one of reflection and sharpening of the other one which shifts towards smaller angles. Similar effect is observed for the angel range 56–57.4 (Fig. 2C). One of the reflections disappears and the other one occurs for smaller angles 2θ .

Table 1. Melting points of synthesized ceramics

Sample composition	Melting point [°C]
$\text{Bi}_4\text{V}_2\text{O}_{11}$	870
$\text{Bi}_4\text{V}_2\text{O}_{11} + 1\% \text{ La}$	885
$\text{Bi}_4\text{V}_2\text{O}_{11} + 2\% \text{ La}$	890
$\text{Bi}_4\text{V}_2\text{O}_{11} + 3\% \text{ La}$	890
$\text{Bi}_4\text{V}_2\text{O}_{11} + 6\% \text{ La}$	908
$\text{Bi}_4\text{V}_2\text{O}_{11} + 8\% \text{ La}$	920
$\text{Bi}_4\text{V}_2\text{O}_{11} + 10\% \text{ La}$	935

Fig. 1. X-ray spectra of the samples made of undoped mass $\text{Bi}_4\text{V}_2\text{O}_{11}$ (0% La) and $\text{Bi}_4\text{V}_2\text{O}_{11}$ doped with 3%, 8%, 10% LaFig. 2. Changes on X-ray spectra connected with phase transition in doped compound: A – angle range 2θ $32\div 34.5$, B – angle range 2θ $36.5\div 38.5$, C – angle range 2θ $56\div 57.5$

According to expectations, the grain growth of the initial material ($\text{Bi}_4\text{V}_2\text{O}_{11}$) connected with longer and longer sintering was observed (from 3 μm for 1 h to 17 μm for 20 h, Fig. 3). Described changes, seen in the spectra of investigated samples, result from doping (1, 2 and 3% La) and prove that α phase in undoped sample exists. It can be also stated that high-temperature γ phase was stabilized as the amount of La dopant was increased. It seems that 3% dopant content is optimum because further increase of La fraction (6–10%) did not cause formation of new chemical compounds.



Fig. 3. Microstructure of undoped $\text{Bi}_4\text{V}_2\text{O}_{11}$ sample (sintering time – from left to right 1 h, 5 h, 10 h)

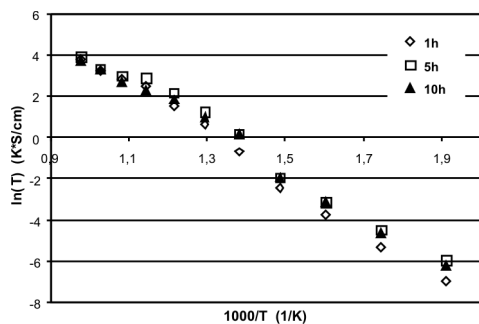


Fig. 4. Arrhenius characteristics of undoped $\text{Bi}_4\text{V}_2\text{O}_{11}$ in dependence on sintering time

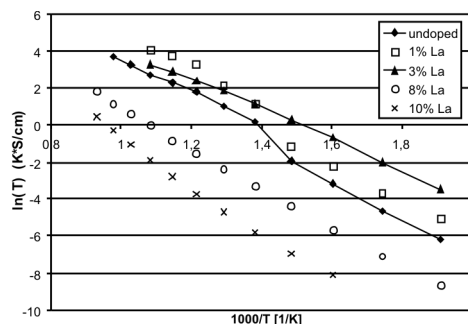


Fig. 5. Arrhenius characteristics of undoped and La doped $\text{Bi}_4\text{V}_2\text{O}_{11}$ measured in air atmosphere

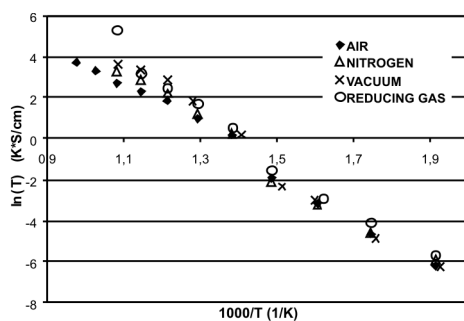


Fig. 6. Arrhenius characteristics of undoped $\text{Bi}_4\text{V}_2\text{O}_{11}$ in dependence on atmosphere

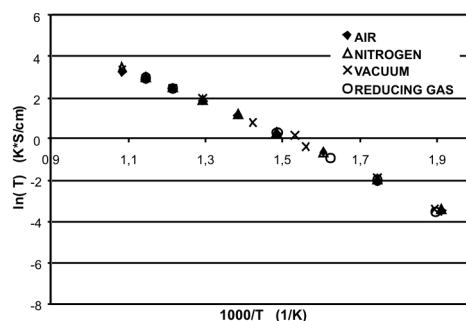


Fig. 7. Arrhenius characteristics of $\text{Bi}_4\text{V}_2\text{O}_{11}$ doped with 3% La in dependence on atmosphere

The measurements of conductivity were performed by use of impedance spectroscopy method in the temperature range 250–650 °C. Arrhenius plots obtained from

calculation performed by taking into account conductivity measurements are presented in Figs. 4–7. A significant influence of sintering time (grain size) on the conductivity of samples was not observed (Fig. 4). The addition of La causes increase of conductivity of the initial material in the full range of temperature. For the compositions with 2% and 3% of La, typical changes of the characteristic slope on the Arrhenius plot were not observed (different slopes for 0% La are responsible for phase changes α – β and β – γ). That could be the proof of the stability of the high temperature γ - $\text{Bi}_4\text{V}_2\text{O}_{11}$ phase with ionic conduction (Fig. 5). Although higher amounts of dopant (6, 8 and 10% La) stabilize γ phase, they also cause significant decrease of electrolyte conductivity. Probably reason are new chemical compounds which block charge transfer. For the further investigations of thermodynamical stability, materials with La content up to 3% were selected.

Based on measurements of the impedance of the initial material, which were made in various atmospheres (air, nitrogen, vacuum, reducing gas – propane–butane), an insignificant increase of conductivity of material in oxygen-free atmospheres for higher temperatures was confirmed (Figs. 6 and 7). This could be caused by increased amount of oxygen vacancies. Significant increase of conductivity in reducing gas atmosphere was observed at 650 °C and was caused by carbon deposition on the sample surface (Fig. 8).



Fig. 8. BIMEVOX before (left) and after measurement in reducing atmosphere (right)

Table 2. Conductivities of BIMEVOX at 400 °C and 650 °C

Sample composition	$\sigma_{400} \times 10^{-3}$ [1/ Ωcm]	$\sigma_{650} \times 10^{-2}$ [1/ Ωcm]
$\text{Bi}_4\text{V}_2\text{O}_{11}$	0.22E-3	1.63
$\text{Bi}_4\text{V}_2\text{O}_{11}$ + 1% La	0.46	6.50
$\text{Bi}_4\text{V}_2\text{O}_{11}$ + 2% La	1.41	2.94
$\text{Bi}_4\text{V}_2\text{O}_{11}$ + 3% La	1.94	2.83
$\text{Bi}_4\text{V}_2\text{O}_{11}$ + 6% La	4.63-6	7.60-4
$\text{Bi}_4\text{V}_2\text{O}_{11}$ + 8% La	1.87-5	1.05-3
$\text{Bi}_4\text{V}_2\text{O}_{11}$ + 10% La	1.40-6	1.66-4

Carbon originated from decomposition gas fuel in the absence of humidification. However, the influence of atmosphere on composition and conductivity of samples

doped with La was not observed. In Table 2, the conductivities measured at 400 °C and 650 °C for: initial Bi₄V₂O₁₁ and doped with 1–10% La are presented.

4. Conclusion

Addition of La₂O₃ increases melting point and conductivity of Bi₄V₂O₁₁ by stabilization of high-temperature, good ionic O²⁻ conductive γ -Bi₄V₂O₁₁ phase. The type of conductivity (ionic or electronic) will be determined in the future works. For materials with La content higher than 3%, the decrease of conductivity was observed.

New electrolytes (up to 3% La content) are thermodynamically stable when placed in pure nitrogen and vacuum (10⁻³ Tr) and during short test (2 h) in pure reducing atmosphere (propane–butane, 650 °C).

The electrical and stability measurements allowed estimating the possibility of applications of elaborated materials in SOFC.

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