



Physicochemical and Transport Properties of BICUVOX-Based Ceramics

A.A. YAREMCHENKO,¹ V.V. KHARTON*² E.N. NAUMOVICH¹ & F.M.B. MARQUES²

¹*Institute of Physicochemical Problems, Belarus State University, 14 Leningradskaya Str., 220080 Minsk, Republic of Belarus*

²*Department of Ceramics and Glass Engineering, University of Aveiro, 3810 Aveiro, Portugal*

E-mail: kharton@cv.ua.pt OR kharton@fhp.bsu.unibel.by

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Abstract. Polycrystalline $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($x = 0, 0.10$ and 0.20) and $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ were prepared by the standard ceramic synthesis technique. Electrical conductivity of the $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ solid solution at temperatures above 500 K is lower in comparison with undoped BICUVOX.10, whereas transport properties of these materials at 370–450 K are close to each other. Doping $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ with praseodymium was found to result in segregating secondary phases and decreasing conductivity and thermal expansion of the ceramics. Oxygen ion transference numbers of the oxides with moderate rare-earth dopant content ($x \leq 0.10$) vary in the range of 0.90–0.99 at 780–910 K, decreasing with increasing temperature. Thermal expansion coefficients of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics were calculated from the dilatometric data to be $(16.1\text{--}18.0) \times 10^{-6} \text{ K}^{-1}$ at 730–1050 K.

Keywords: BICUVOX, ionic conductivity, transference numbers, thermal expansion, electrode

1. Introduction

Oxide compounds, derived from $\text{Bi}_4\text{V}_2\text{O}_{11}$ by partial substitution of vanadium with copper and referred to as BICUVOX, are characterized by a high oxygen ionic conductivity at moderate temperatures [1–5]. Due to this, such materials have important potential applications in high-temperature electrochemical devices such as oxygen generators, sensors and oxygen separation membranes [1,2,6,7]. Crystal lattice of the oxides of the BICUVOX family refers to the Aurvillius series, consisting of alternating $\text{Bi}_2\text{O}_2^{2+}$ and perovskite-like $\text{VO}_{5.5}$ layers. Oxygen vacancies located in the perovskite layers of bismuth vanadate are responsible for the ionic conduction. The parent compound, $\text{Bi}_4\text{V}_2\text{O}_{11}$, was ascertained to exhibit three structurally distinct α , β and γ phases that form due to ordering oxygen vacancies with decreasing temperature [8]. The high-temperature tetragonal γ polymorph, which is of main interest as the solid electrolyte, can be stabilized down to room temperature by doping with copper, resulting in

unusually high ionic conductivity at 500–800 K [1,3,4,9]. The solid solutions of $\text{Bi}_2\text{V}_{1-x}\text{Cu}_x\text{O}_{5.5-\delta}$ have been reported to form in the composition range of $0.07 \leq x \leq 0.12$, whereas the transport properties do not vary very much over this substitution range [10]. Oxygen ion transference numbers of $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ (so called BICUVOX.10), determined by the Faradaic efficiency measurements, vary in the range of 0.85–1.0 [11,12].

The present work was aimed at studying properties of $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics doped with lanthanum and praseodymium. Our attention to these materials was caused, firstly, by a possible formation of such oxides in the diffusion layers between BICUVOX solid electrolytes and perovskite electrodes containing rare-earth elements. Perovskite-type solid solutions such as $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ have been reported to be promising electrode materials for electrochemical cells with $\text{Bi}_4\text{V}_2\text{O}_{11}$ -based electrolytes [1,13]. The ceramics derived from bismuth vanadate possess extremely high chemical reactivity [1,13,14], and interdiffusion of the electrolyte and

electrode materials in the course of operating electrochemical devices seems to be very probable. On the other hand, doping with lanthanum was found to increase temperature, necessary for sintering gas-tight ceramics of the $\text{Bi}_2(\text{V},\text{M})\text{O}_{5.5-\delta}$ ($\text{M} = \text{Cu}, \text{Ni}$) ceramics [15], and, therefore, its melting point. Hence, partial substituting of bismuth with rare-earth oxides may be useful from viewpoint of reducing reactivity of the bismuth vanadate-based electrolytes. The upper stability limit of the single $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ -type phase in the oxide system $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ was estimated to correspond to the x values of approximately 0.10–0.15 [15]. Further additions of lanthanum lead to the LaVO_4 phase segregation, increasing electronic conduction and decreasing ionic conductivity of the ceramics [15].

A particular emphasis in this work was given to determination of the ionic transport parameters of BICUVOX-based ceramics by measuring e.m.f. of the oxygen concentration cells. Using the Faradaic efficiency technique [11,15] for determining transference numbers may result in lower measured oxygen transference numbers in comparison with their true values, caused by a partial reduction of a sample and increasing electronic conductivity due to the applied electrical potential difference. The BICUVOX ceramics can be reduced at relatively low voltages [14]. Therefore, determination of the transference numbers at low electrical or oxygen chemical potential gradients seems to be preferable in this case. The present paper contains also refined data on thermal expansion and electrical conductivity of $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($x = 0.10$ and 0.20) ceramics as compared to that published previously [15].

2. Experimental

2.1. Preparation and Characterization Methods

Powders of $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($x = 0, 0.10$ and 0.20) and $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ were prepared by the standard ceramic synthesis route. Starting materials and preparation details were described elsewhere [15]. After pressing, the ceramic specimens were sintered at 1080–1170 K in air for 15–40 h. The density of the ceramics was from 91 to 94% in relation to the theoretical density calculated from the results of X-ray diffraction (XRD) data.

The prepared oxides were characterized by XRD, scanning electron microscopy (SEM), X-ray fluorescence analysis (XFA), atomic emission spectroscopy (AES) and dilatometry. The experimental techniques and equipment for XRD, AES, XFA, SEM and measuring thermal expansion were described in detail earlier [15–21]. Three-point bend strength of the ceramic specimens ($36 \times 4 \times 3 \text{ mm}^3$) was studied at room temperature using an INSTRON-1195 apparatus with the span length of 20 mm and the ramp speed of 0.5 mm/min.

Electrical conductivity was measured by the 2-probe ac method in the temperature range of 370–1070 K in air. For these measurements, both constant-frequency technique described in [16] and impedance spectroscopy [22] were used. The impedance spectra were obtained using a HP 4284A analyzer within the frequency range of 20 Hz to 1 MHz. The typical impedance spectra are presented in Fig. 1. The high-frequency parts of the spectra, which appear below the real axis at temperatures above 670–770 K, have been attributed to inductive effects inherent to the experimental setup [23].

2.2. Oxygen Ion Transference Number Measurements

The ion transference numbers of the $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($\text{Ln} = \text{La}, \text{Pr}$), ceramics were determined from e.m.f. of the oxygen concentration cell:

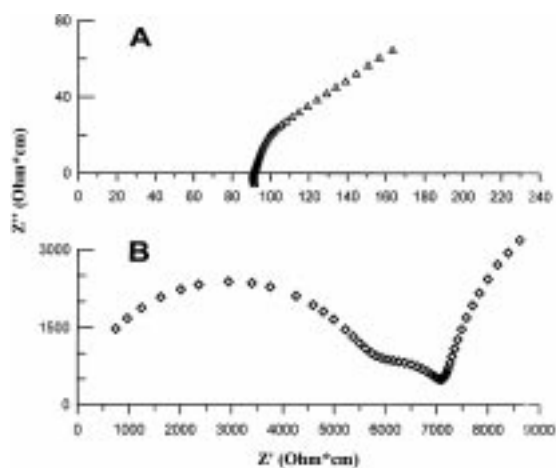
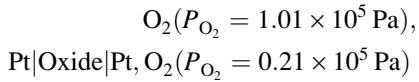


Fig. 1. Impedance spectra of $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ with Pt-electrodes in air at 673 K (A) and 473 K (B).



Platinum electrodes were deposited onto the ceramic discs using a paste, containing highly dispersed Pt and organic binder, and then annealed at 970–1000 K for 15–30 min. The experimental technique of the transference number determination has been described elsewhere [16]. The measuring cell consisted of platinum current collectors and dense alumina tubes attached to a disk sample, separating electrode volumes. In the measurement course, corresponding gases (oxygen or air) were continuously supplied onto the electrodes for maintaining steady oxygen chemical potential gradient. Before supplying into the cell, the gases were passed over Pt/Al₂O₃ catalysts heated up to 1070 K in order to avoid any effect of organic impurities, which might penetrate into the gas communications, on the measured quantities. The catalysts produced by the Institute of Catalysis (Novosibirsk, Russia) were used in the cell.

In order to avoid an effect of the electrode polarization resistance on measured transference numbers, we used Gorelov's modification of the e.m.f. method, which refers to studying e.m.f. of the concentration cells as a function of resistance of the external load closing the circuit [24,25]. Gorelov [24] showed that the polarization resistance affects the measured e.m.f. of electrochemical cells with mixed ionic-electronic conductors, as illustrated by Fig. 2a. Electrical current *I*, flowing through such a cell, can be expressed by the formula:

$$I = \frac{E_{\text{theor}} - \eta}{R_o + R_e} = \frac{E_{\text{exp}}}{R_e} \quad (2)$$

where *E_{exp}* is the measured e.m.f. value, *E_{theor}* is the theoretical e.m.f. defined by the Nernst equation, *η* is the sum of the electrode overpotentials, *R_o* and *R_e* are the partial oxygen ionic and electronic resistances of the mixed conductor, respectively. If the overpotentials are low

$$\eta = I \cdot R_\eta \quad (3)$$

where *R_η* is the total polarization resistance. The oxygen ion transference number (*t_o*) is defined as

$$t_o = \frac{\sigma_o}{\sigma_o + \sigma_e} = \frac{R_e}{R_o + R_e} \quad (4)$$

where *σ_o* and *σ_e* are the partial oxygen ionic and

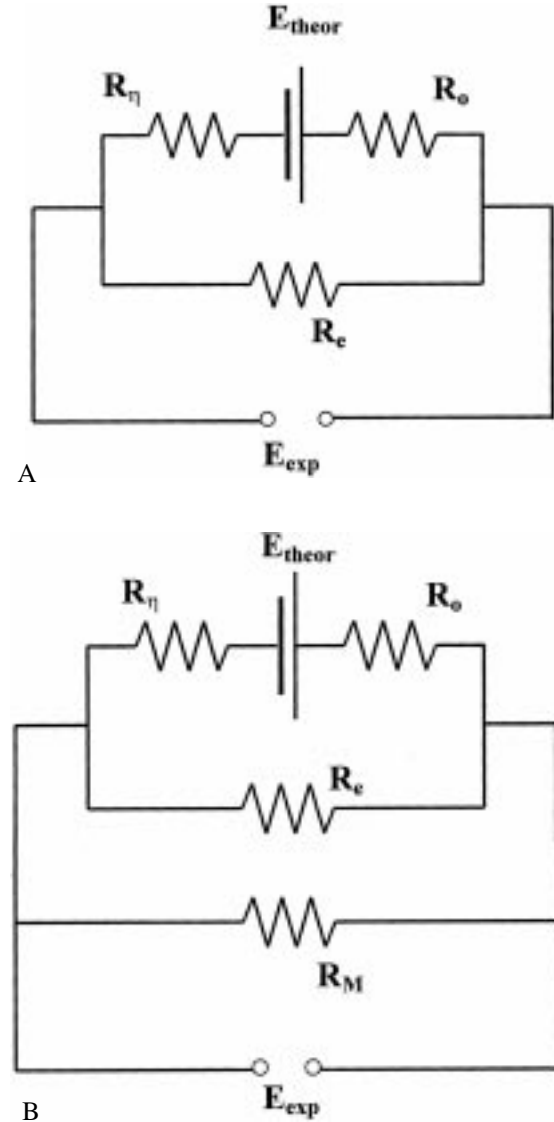


Fig. 2. Equivalent circuit of a mixed conductor placed under oxygen chemical potential gradient (A), and the cell for the transference number measurements (B).

electronic conductivities, respectively. Substituting Eqs. (3) and (4) into Eq. (2), one can obtain

$$E_{\text{exp}} = t_o \cdot E_{\text{theor}} \cdot \left[1 + \frac{R_\eta}{R_o + R_e} \right]^{-1} \quad (5)$$

Therefore, determining *t_o* of mixed conductors as a ratio between measured and theoretical e.m.f. values may result in underestimated ion transference numbers due to presence of the electrode polarization

resistance. Gorelov [24] proposed to connect a variable resistor to the electrodes (Fig. 2b) and to study e.m.f. as a function of its resistance (R_M). In this case

$$\frac{E_{\text{theor}}}{E_{\text{exp}}} - 1 = (R_o + R_\eta) \cdot \left[\frac{1}{R_e} + \frac{1}{R_M} \right] \quad (6)$$

The dependences of e.m.f. of the cell (1) on the external load resistance were studied in the range of R_M from 0.1 to 10^5 Ohm. The values of $(1/R_e)$ were obtained by fitting of the linear dependence

$$\frac{E_{\text{theor}}}{E_{\text{exp}}} - 1 = A \cdot \left(\frac{1}{R_M} \right) + B \quad (7)$$

where A and B are the regression parameters,

$$A = R_o + R_\eta$$

$$B = \frac{R_o + R_\eta}{R_e} = \frac{A}{R_e}$$

The oxygen ion transference numbers were calculated by

$$t_o = 1 - t_e = 1 - \frac{R}{R_e} \quad (8)$$

where t_e is the electron transference number, and R is the total resistance of the sample, measured independently using ac. The transference numbers were studied in the temperature range of 760–910 K. Figure 3 gives an example of the dependence of Eq. (6), obtained for cell (1) with a sample of $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ at 908 K.

3. Results and Discussion

3.1. Characterization of the Ceramics

XRD results showed formation of the tetragonal phase, isostructural to $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$, for all the prepared materials. The $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ and $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics were single phase. For $\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$, traces of the second LaVO_4 phase were observed in the XRD patterns, which is in agreement with the data on the solid solution formation range in the $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ system reported elsewhere [15]. XRD patterns of $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ exhibited traces of the BiVO_4 phase and one unidentified peak, corre-

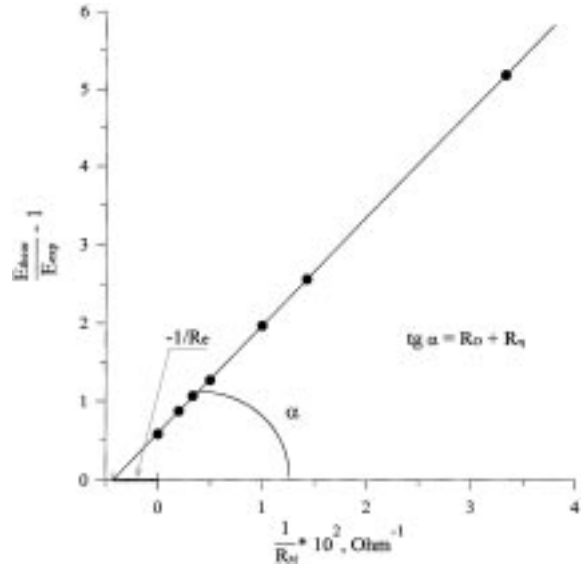


Fig. 3. Measured e.m.f. of the cell (1) as a function of reciprocal R_M , presented according to Eq. (6), for $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics at 908 ± 2 K. The solid line corresponds to the fitting results using Eq. (7) as a regression model.

sponding to the interplanar spacing of $d = 0.386$ nm. This suggests that the concentration range of forming solid solutions $(\text{Bi,Pr})_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ is more narrow in comparison with the $(\text{Bi,La})_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ system, caused probably by the higher average oxidation state of praseodymium cations as related to lanthanum. The tetragonal unit cell parameters of the oxides are listed in Table 1.

Table 1 presents also thermal expansion coefficients (TECs) calculated by fitting of the dilatometric data. The dilatometric curves of the BICUVOX-based materials exhibit a considerable non-linearity (Fig. 4), which causes relatively high error in the TEC values. TECs of the $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($x = 0 - 0.20$) ceramics are close to each other, varying in the range of $(14.9 - 15.3) \times 10^{-6} \text{ K}^{-1}$ at temperatures of 300–700 K and $(17.7 - 18.0) \times 10^{-6} \text{ K}^{-1}$ at 730–1050 K; doping by lanthanum leads to a slight decrease in the thermal expansion. The break in the dilatometric curves near 700 K is associated, most probably, with the transition from partially ordered (so called γ^{-1} -phase) to disordered crystal lattice [26]. This phase transition is accompanied with a decrease in the activation energy for ionic conduction [26]. Such behavior can be qualitatively explained in terms of the phenomenological theory of ionic transport [27]

Table 1. Properties* of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics

Composition	Parameters of the unit cell		Mean values of TECs	
	a_t , nm	c_t , nm	T , K	$\bar{\alpha} \cdot 10^6$, K^{-1}
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	0.3921	1.5458	300–730 730–1030	15.3 ± 0.2 18.0 ± 0.4
$\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	0.3931	1.5423	300–640 640–1000	15.0 ± 0.2 17.7 ± 0.6
$\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	0.3940	1.5473	300–670 670–1060	14.9 ± 0.2 17.7 ± 0.3
$\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	0.3925	1.5453	300–700 700–1040	10.5 ± 0.5 16.1 ± 0.7

* $\bar{\alpha}$ is the thermal expansion coefficient (TEC) calculated from dilatometric data and averaged in the given temperature range.

showed that the mobility of ionic defects increases with thermal expansion of the crystal. The TEC value of $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ in the low-temperature region (300–700 K) was ascertained to be significantly lower than that of La-substituted BICUVOX ceramics, whereas increasing temperature results in increasing TEC of $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ up to $16.1 \times 10^{-6} \text{ K}^{-1}$. Notice that doping with praseodymium leads also to increasing non-linearity of the dilatometric curves (Fig. 4).

Mechanical strength of the BICUVOX-based materials is essentially worse as compared to well-known solid-electrolyte ceramics of yttria-stabilized zirconia and doped lanthanum gallate (Table 2). The poor mechanical properties may complicate practical

applications of BICUVOX. Substitution of bismuth with lanthanum provides a definite increase of the bending strength. It should be mentioned, however, that such an improvement is comparable to the experimental error of the flexural strength determination.

3.2. Interaction of the Solid Electrolyte and Electrode Materials

Testing stability of the BICUVOX-based electrolytes in contact with different electrode materials was performed by studying conductivity of the ceramics as a function of temperature and time (Figs. 5–7). For the tests, we used ceramic specimens in the shape of bars with electrodes applied onto the both end faces. In the electrode preparation course, pastes consisting of an organic binder and highly-dispersed metallic platinum, silver or $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ solid solution were deposited onto the samples and then annealed in air for 15–30 min. Details on the synthesis of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ cobaltite were published elsewhere [19]. Annealing temperatures were chosen to be minimum, necessary to provide sufficient mechanical strength of the electrodes: 970–1000 K for Pt, 1010–1030 K for $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$, and 920–940 K for Ag.

The results of the tests showed instability of silver electrodes in contact with the BICUVOX-based electrolytes. Indeed, measured electrical conductivity values of the $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics with Ag-electrodes decreased more than 10 times during first 50 h of the tests (Fig. 7). Such results are similar to our previous data [31] showed a chemical interaction of metallic silver with fluorite-type oxides on the basis of $\delta\text{-Bi}_2\text{O}_3$. The resistance of the samples with platinum electrode layers was found to be

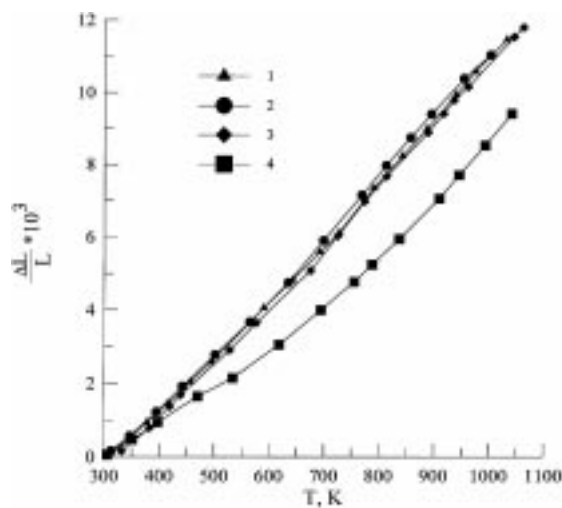


Fig. 4. Dilatometric curves of $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ with (1), $x = 0$, (2), $x = 0.10$, (3), $x = 0.20$, and (4), $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ in air.

Table 2. Flexural strength of oxide solid-electrolyte ceramics

Composition	Flexural strength, MPa	Reference
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	83 ± 16	This work
$\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	97 ± 12	This work
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$	162	[28]
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$	~ 150	[29]
$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$	~ 240	[30]

essentially independent of time for more than 200 h (Fig. 7). As a result, the conductivity values, obtained using Ag-electrodes after their fabrication, are significantly lower as related to the data obtained with Pt-electrodes (Figs. 5 and 6). For comparison, Fig. 5 presents literature data on conductivity of BICUVOX.10. Using platinum electrodes allowed us to obtain the conductivity values close to the literature results. The resistance of the sample with electrodes of lanthanum-strontium cobaltite was also time-independent, but was higher with respect to the ceramics with Pt-electrodes (Figs. 6 and 7). This indicates possible interdiffusion between cobaltite and the solid-electrolyte material during electrode preparation.

Thus, electrodes of metallic platinum and $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ exhibit sufficient stability in contact with BICUVOX-based solid electrolytes at temperatures below 800 K. In the case of lanthanum-strontium cobaltite, further developments

of the electrode fabrication technology are necessary in order to avoid interaction between the materials in the preparation course, which may result in increasing resistance of the electrochemical cells.

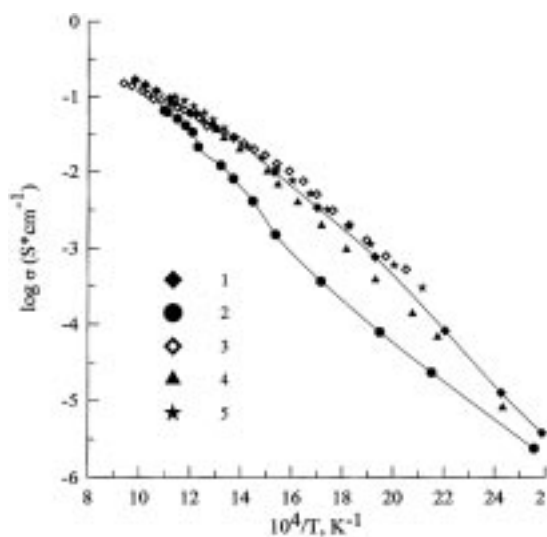


Fig. 5. Temperature dependence of conductivity of BICUVOX.10 ceramics: (1), Pt-electrodes, this work; (2), Ag-electrodes, this work; (3), [3]; (4), [4]; (5), [32].

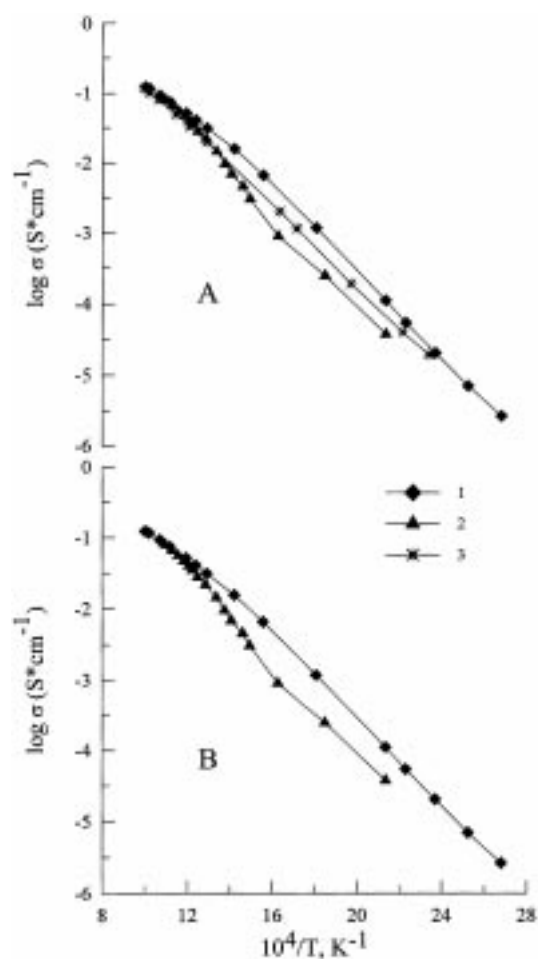


Fig. 6. Temperature dependence of the electrical conductivity of $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ (A) and $\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ (B): (1), Pt-electrodes; (2), Ag-electrodes; (3), electrodes of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$.

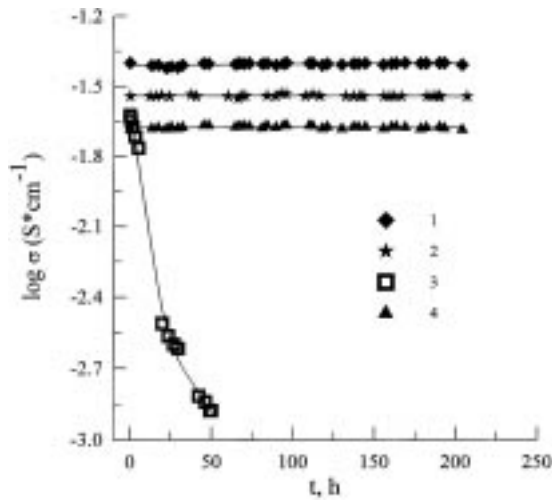


Fig. 7. Time dependence of the electrical conductivity of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ at 780 ± 3 K: (1), $x = 0$, Pt-electrodes; (2), $x = 0.10$, Pt-electrodes; (3), $x = 0.10$, Ag-electrodes; (4), $x = 0.10$, electrodes of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$.

3.3. Electrical Conductivity and Ion Transference Numbers

Temperature dependence of the electrical conductivity of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ materials is shown in Fig. 8. The conductivity of $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ at temperatures above 500 K is slightly lower than that of BICUVOX.10; at lower temperatures the conductivity values for the doped and undoped materials are close to each other. Transport properties of the $\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics are significantly worse due to the secondary LaVO_4 phase segregation. Doping BICUVOX with praseodymium was found to result in lower conductivity values with respect to substituting bismuth with lanthanum, caused by both second phase formation and decreasing oxygen vacancy concentration when Pr^{4+} cations are incorporated into the bismuth sublattice. The activation energy for electrical conductivity (E_a) were calculated using the standard Arrhenius model:

$$\sigma = \frac{A_0}{T} \cdot \exp\left[-\frac{E_a}{RT}\right] \quad (9)$$

where A_0 is the pre-exponential factor. Parameters of the regression model Eq. (9) are added in Table 3. The activation energy values lie in the range of 45–58 kJ/mol at high temperatures (700–1050 K) and

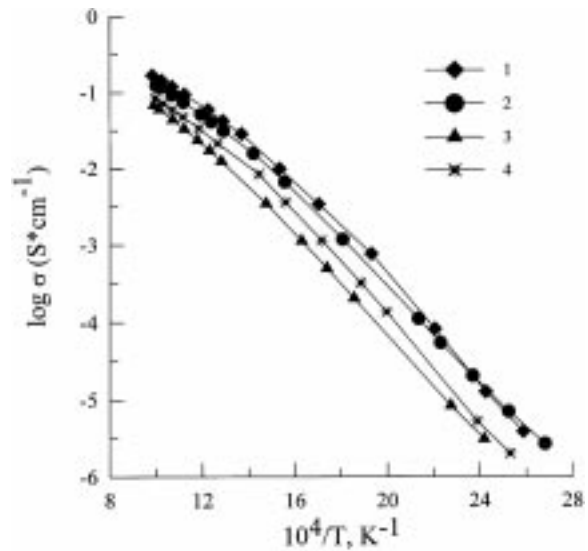


Fig. 8. Temperature dependence of the electrical conductivity of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics in air: (1), BICUVOX.10; (2), Ln = La, $x = 0.10$; (3), Ln = La, $x = 0.20$; (4), Ln = Pr, $x = 0.10$. In all cases Pt-electrodes were used.

increase up to 62–69 kJ/mol with decreasing temperature. The increase in the activation energy is associated with the partial ordering of the oxygen sublattice [26].

Figure 9 presents temperature dependence of the grain bulk and grain boundary resistivities of $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ and $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics, estimated from the impedance spectroscopy data using the conventional brick-layer model. The separation of these contributions to the total resistance was possible only at temperatures below 550 K. The activation energy for the grain boundary resistivity is significantly higher than that for the grain bulk, which is in agreement with the literature data on other oxygen ionic conductors (for example, [21,33]). As a result, the grain boundary contribution to the total resistance becomes significant only at temperatures as low as 420 K. Note that the behaviour of the grain boundary resistivity of undoped and La-substituted BICUVOX is similar. This indicates an uniform distribution of lanthanum in the grain bulk, because one could expect a higher grain boundary contribution in case of segregation of either lanthanum oxide or lanthanum vanadate phase at the grain boundaries.

Oxygen ion transference numbers of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$, measured by the modified e.m.f. method, vary from 0.90 to 0.99 at 780–

Table 3. Regression parameters* of temperature dependence of the electrical conductivity of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics in air

Composition	T, K	E_a , kJ/mol	$\ln(A_0)$ (S/cm)	ρ
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	370–730	66 ± 2	14.1 ± 0.7	0.994
	730–1020	45 ± 1	10.6 ± 0.2	0.998
$\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	370–700	62.4 ± 0.8	13.1 ± 0.2	0.999
	700–1010	48 ± 1	10.6 ± 0.1	0.998
$\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	410–680	66.7 ± 0.7	12.7 ± 0.2	0.999
	680–1010	58 ± 2	11.2 ± 0.2	0.997
$\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	390–690	69 ± 1	13.8 ± 0.3	0.999
	690–1010	49.9 ± 0.7	10.4 ± 0.1	0.999

* E_a is the activation energy for electrical conductivity.

ρ is the correlation coefficient of the regression model Eq. (9).

910 K (Table 4). These values are sufficiently close to the literature data [7,11]. Increasing temperature results in increasing electronic conductivity which occurs probably via hopping electron charge carriers between transition metal cations ($\text{Cu}^{2+/1+}$ and $\text{V}^{5+/4+}$). The values of the ion transference numbers, determined in our previous work [15] from the Faradaic efficiency results to be 0.90–0.93 at 740–780 K, were probably underestimated due to a partial reducing of the samples by the applied voltage.

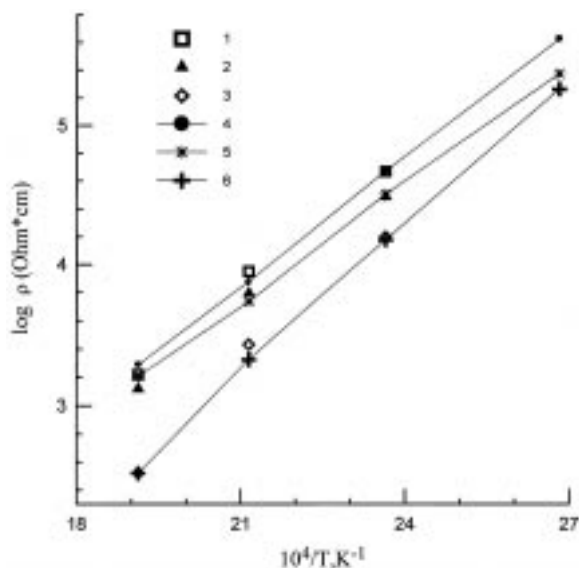


Fig. 9. Temperature dependence of the specific electrical resistivity of $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ (curves 1–3) and $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ (4–6): 1 and 4—total resistivity; 2 and 5—grain bulk resistivity; 3 and 6—grain boundary resistivity.

4. Conclusions

Polycrystalline $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($x = 0, 0.10$ and 0.20) and $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ were prepared by the standard ceramic synthesis route. Electrical conductivity of the $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ solid solution at temperatures above 500 K is lower in comparison with undoped BICUVOX.10, whereas transport properties of these materials at 370–450 K are close to each other. Impedance spectroscopy data suggest probable uniform distribution of lanthanum in the grain bulk of $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$. Substitution of bismuth with lanthanum was found to result in a slight improvement in the mechanical strength of the BICUVOX-based ceramics. Segregating secondary phases of LaVO_4 in the case of $\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ and BiVO_4 for $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ leads to decreasing electrical conductivity. Oxygen ion transference numbers of the oxides with moderate rare-earth dopant content ($x \leq 0.10$) were measured by modified e.m.f. method to be 0.90–0.99 at 780–910 K, decreasing with increasing temperature.

Thermal expansion coefficients of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ vary in the range $(16.1\text{--}18.0) \times 10^{-6} \text{K}^{-1}$ at 730–1050 K. At 300–700 K TECs of the La-substituted materials are $(14.9\text{--}15.3) \times 10^{-6} \text{K}^{-1}$, whilst doping with praseodymium leads to the TEC value as low as $(10.5 \pm 0.5) \times 10^{-6} \text{K}^{-1}$.

Testing BICUVOX-based ceramics in contact with different electrode materials showed their interaction with metallic silver, resulting in a dramatic degradation in conductivity of the electrochemical cells. Electrodes of platinum and perovskite-type

Table 4. Transference numbers of the $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics determined by the e.m.f. method

Composition	T, K	Oxygen ion transference numbers*	
	(± 1 K)	t_o	ρ
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	908	0.903 ± 0.002	0.9999
	850	0.979 ± 0.005	0.9999
	785	0.98 ± 0.02	0.9967
$\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	908	0.921 ± 0.002	0.9999
	846	0.989 ± 0.006	0.9996
$\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	908	0.938 ± 0.002	0.9999
	846	0.98 ± 0.01	0.9990

* The transference number errors and the correlation coefficient (ρ) were calculated using the regression model Eq. (7).

$\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ were found to exhibit sufficient stability, but further developments of the cobaltite electrode fabrication technology are desirable in order to avoid interdiffusion of the materials in the preparation course.

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