

Transport properties of doped BICUVOX ceramics

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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. The total electrical 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 undoped BICUVOX.10, but transport properties in the temperature range 370 – 450 K are similar. Doping BICUVOX.10 with praseodymium led to the formation of impurity phases, and to both lower conductivity and thermal expansion of ceramic samples. Oxygen-ion transference numbers of phases with moderate rare-earth dopant content ($x \leq 0.10$) vary in the range 0.90 – 0.99 at 780 – 910 K and decrease with increasing temperature. Thermal expansion coefficients calculated from the dilatometric data for $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics are $(16.1 - 18.0) \times 10^{-6} \text{ K}^{-1}$ at 730 – 1050 K.

Key words: BICUVOX.10, ceramic synthesis, ionic conductivity, transference number, thermal expansion

Propiedades de transporte de cerámicas Bicuvox dopadas

$\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ($x = 0, 0.10$ and 0.20) y $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ policristalinos fueron preparados por síntesis cerámica convencional. La conductividad eléctrica total de $\text{Bi}_{2-x}\text{La}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ a temperaturas superiores a 500K es ligeramente menor que la correspondiente a BICUVOX.10 no dopada, pero las propiedades de transporte en el rango de temperaturas 370-450K son similares. Dopando BICUVOX.10 con praseodimio produce la formación de fases secundarias y la reducción de la conductividad y la expansión térmica de las muestras cerámicas. El número de transporte del ión sin oxígeno de fases con un contenido en tierra rara moderado como dopante ($x \leq 0.10$) varía en el rango 0.90-0.99 a 780-910K y disminuye con el aumento de la temperatura. Los coeficientes de expansión térmicos calculados a partir de los datos dilatométricos para cerámicas $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ son $(16.1 - 18.0) \times 10^{-6} \text{ K}^{-1}$ a 730 – 1050 K.

Palabras clave: Bicuvox.10, síntesis cerámica, conductividad iónica y número de transferencia, expansión térmica

1. INTRODUCTION

Oxide compounds derived from $\text{Bi}_4\text{V}_2\text{O}_{11}$ by partial substitution of vanadium with copper, commonly referred to as BICUVOX, possess high oxygen ionic conductivity at moderate temperatures (1-6). These materials are, therefore, of interest for numerous electrochemical applications, such as oxygen generators, sensors and oxygen-separation membranes (3,7,8). The BICUVOX series belong to the Aurivillius family of phases, the crystal structure of which is composed of alternating layers of $\text{Bi}_2\text{O}_2^{2+}$ and perovskite-like layers of $\text{VO}_{3.5}^{2-}$. Ionic transport occurs via oxygen-anion-hopping between oxygen vacancies located in the perovskite layers. The parent compound, $\text{Bi}_4\text{V}_2\text{O}_{11}$, exhibits three structurally distinct phases, α , β and γ ; the three phases differ by the manner in which the oxygen vacancies order with decreasing temperature (5). The high-temperature, tetragonal γ polymorph is the best solid electrolyte, and can be stabilised down to room temperature by doping with copper, resulting in unusually high ionic conductivity between 500 and 800 K (1,2,4). Solid solution formation in the $\text{Bi}_2\text{V}_{1-x}\text{Cu}_x\text{O}_{5.5-\delta}$ series has been reported for a composition range of $0.07 \leq x \leq 0.12$, with little change in transport properties throughout this range (1). 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 Faradaic efficiency measurements, vary from 0.85 to 1.0 (3,6). The present work focuses on the properties of $\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics doped with lanthanum and praseodymium.

2. EXPERIMENTAL PROCEDURE

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 solid-state reaction using two different methods employing different starting materials and thermal history. (Hereafter, compositions are designated by the abbreviations listed in Table 1.). Method I involved dissolving stoichiometric amounts of high-purity $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, CuC_2O_4 , NH_4VO_3 and Pr_6O_{11} in a 0.1 M aqueous solution of nitric acid with subsequent drying and thermal decomposition of the products, performed by a slow heating of the mixtures up to 770 – 800 K in air. Reaction took place in air in a temperature range of 920 – 1050 K for 20 - 25 hours with several intermediate regrindings.

TABLE I. ABBREVIATIONS AND SINTERING TEMPERATURE OF GAS-TIGHT $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-8}$ CERAMICS

Composition	Abbreviation	Temperature of sintering (± 15 K)
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-8}$	BC0 (BICUVOX.10)	1030
$\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-8}$	BLC1	1090
$\text{Bi}_{1.80}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-8}$	BLC2	1110
$\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-8}$	BPC1	1070

The second synthesis procedure (Method II), used to prepare samples of BC0 and BLC1, consisted of ball-milling stoichiometric mixtures of dried La_2O_3 , Bi_2O_3 , V_2O_5 and CuO and annealing at 920 – 1040 K for approximately 45 hours with intermediate regrinding. In all cases, the rates of heating and cooling in the course of preparation did not exceed 4-5 K/min. The total amount of each of the oxides synthesized was 45 – 60 g in the case of Method I and 20 – 25 g for Method II. The powders were then pressed (350 – 500 MPa) into the shape of disks of various diameters and bars ($4 \times 4 \times 30 \text{ mm}^3$) and sintered in air for 10 – 25 hours; final firing temperatures are listed in Table 1.

The reaction products were characterised by X-ray diffraction (XRD), X-ray fluorescence analysis (XFA), scanning electron microscopy (SEM), emission spectroscopic analysis, infrared (IR) absorption spectroscopy and dilatometry. Experimental procedures for the characterisation, including determination of the oxygen-ion transference numbers by the e.m.f. method, have been reported elsewhere (6,9-14). The spectroscopic analysis showed no deviations in the cation composition of the ceramics with respect to their chemical formulas within the experimental error limits; the total concentration of impurities was found to be less than 0.01 at%. Lattice parameters for the BC0 and BLC1 phases, prepared by Method II, were refined from the x-ray powder data using the program FULLPROF (15) in pattern-matching mode; the data were

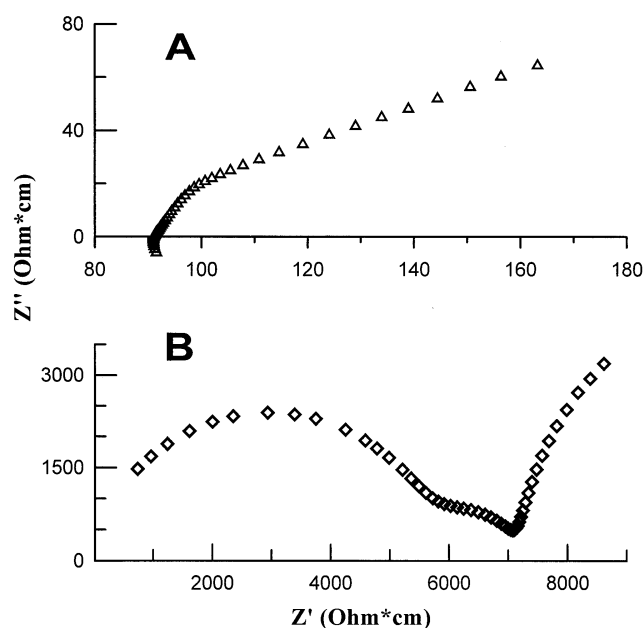


Fig.1. Impedance spectra of BLC1 ceramics prepared by method II in air at 673 K (A) and 473 K (B).

TABLE II. PROPERTIES OF $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-8}$ CERAMICS

Oxide	Unit cell parameters		Mean values of thermal expansion coefficients		Oxygen ion transference numbers averaged in oxygen/air gradient	
	a, nm	c, nm	T, K	$\bar{\alpha} \cdot 10^6, \text{K}^{-1}$	T, K	t_o
BC0	0.3921	1.5458	300 – 730	15.3 ± 0.2	908	0.903 ± 0.002
	(0.39234(1))	(1.54674(6))	730 – 1030	18.0 ± 0.4	850	0.979 ± 0.005
BLC1	0.3931	1.5423	300 – 640	15.0 ± 0.2	908	0.921 ± 0.002
	(0.39315(2))	(1.54745(8))	640 – 1000	17.7 ± 0.6	846	0.989 ± 0.006
BLC2	0.3940	1.5473	300 – 670	14.9 ± 0.2		
			670 – 1060	17.7 ± 0.3		
BPC1	0.3925	1.5453	300 – 700	10.5 ± 0.5	908	0.938 ± 0.002
			700 – 1040	16.1 ± 0.7	846	0.98 ± 0.01

collected over the range $10^\circ \leq \theta \leq 110^\circ$ on a Rigaku Geigerflex diffractometer equipped with $\text{CuK}\alpha$ radiation. Electrical conductivity was measured by the 2-probe AC method in a temperature range of 370 - 1070 K in air. For this, electrodes of highly dispersed platinum were deposited onto ceramic samples and annealed between 970 and 1000 K. Both constant-frequency (described in Ref.(9)) and impedance-spectroscopy measurements were carried out(10) using an HP 4284A analyzer with a frequency range of 20 Hz to 1 MHz. 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, are attributable to inductive effects inherent to the experimental set-up. Analysis of the impedance

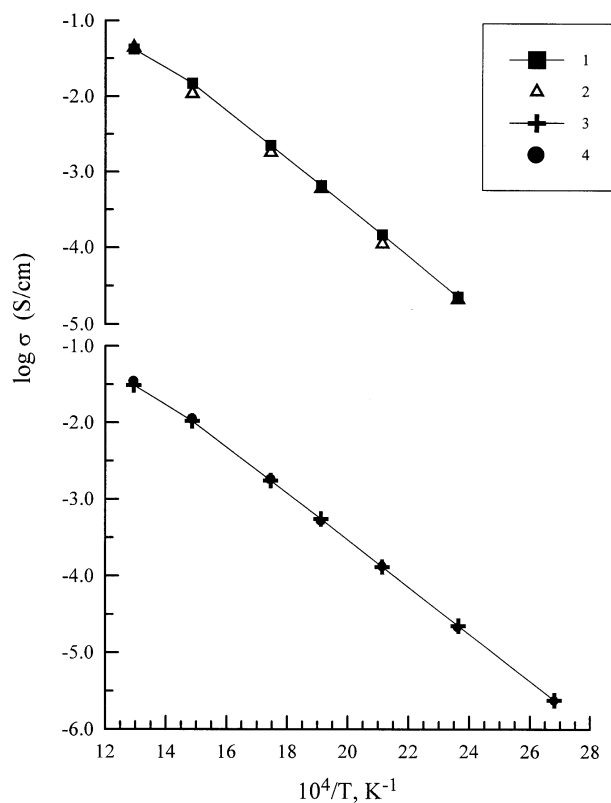


Fig.2. Temperature dependence of the total electrical conductivity of BC0 (1,2) and BLC1 (3,4) in air: for 1 and 3, samples were prepared by the method I; for 2 and 4, method II was employed.

TABLE III. 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
$\text{Bi}_{1.90}\text{La}_{0.20}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$	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

* ρ is the correlation coefficient of the regression model Eq.(1)

spectra was performed using a conventional brick-layer model to estimate grain-bulk and grain-boundary contributions to the total conductivity.

3. RESULTS AND DISCUSSION

3.1. Phase composition and crystal structure

Analysis of the XRD patterns of the materials, prepared by Method I, indicated that the tetragonal phase, isostructural to $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$, was formed for all compositions. 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; in the case of BLC2, however, traces of LaVO_4 were observed in the XRD pattern. These results agree with our previous 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 (6). SEM studies the BC0 and BLC1 samples confirmed absence of impurity phases. The X-ray diffraction pattern 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 BiVO_4 phase and one unidentified peak at approximately $2\theta = 23^\circ$ (CuK_α - radiation). This suggests that the concentration

range of $(\text{Bi,Pr})_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ solid-solution formation is narrower than that of the $(\text{Bi,La})_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ system, most probably as a result of the higher average oxidation state of praseodymium in comparison to lanthanum. The tetragonal unit-cell parameters (a and c) of the oxides prepared by Method I are listed in Table 2. Refinement by pattern matching of the lattice parameters of BC0 and BLC1, prepared by Method II, confirmed the symmetry of both phases to be tetragonal (S.G. I4/mmm); unit-cell data for these phases are given in Table 2 in parentheses. Further structural details on these compositions will be published elsewhere. The IR absorption spectra of La-doped BICUVOX and their relationships with the crystal lattice parameters have been reported earlier (6).

3.2. Electrical characterisation

Figure 2 presents the temperature dependence of the total electrical conductivity of BICUVOX.10 and $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ ceramics, prepared by the different routes. The conductivity values are independent of the preparation method within the limits of experimental error, suggesting that there is a negligible effect of the synthesis conditions on the electrical properties. Analysis of the impedance spectra (e.g. Fig.1) showed that deconvolution of grain-bulk and grain-boundary contributions from the total resistance was possible only at temperatures below 550 K. The activation energy of the grain-boundary resistivity is significantly higher than that of the grain bulk, a typical feature of many oxygen ionic conductors. Consequently, in this case the grain-boundary contribution to the total resistance becomes significant only at temperatures as low as 420 K. The values of both grain-boundary and grain-bulk resistivity of BLC1 ceramics are similar to corresponding values for undoped BICUVOX.10. One can, thus, assume that there is a uniform distribution of lanthanum in the grain bulk, since a higher grain-boundary contribution would be expected in the case of segregation of either lanthanum-oxide or lanthanum-vanadate phase at the grain boundaries.

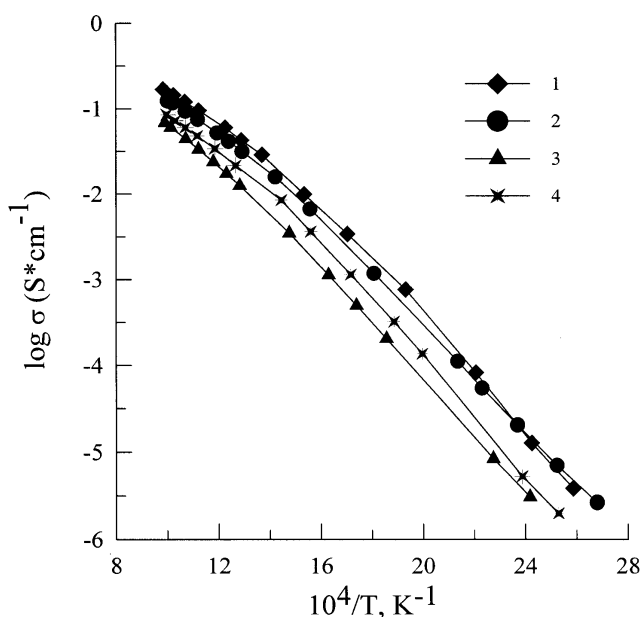


Fig.3. Temperature dependence of the electrical conductivity in air: (1), BC0, (2), BLC1, (3), BLC2, (4), BPC1.

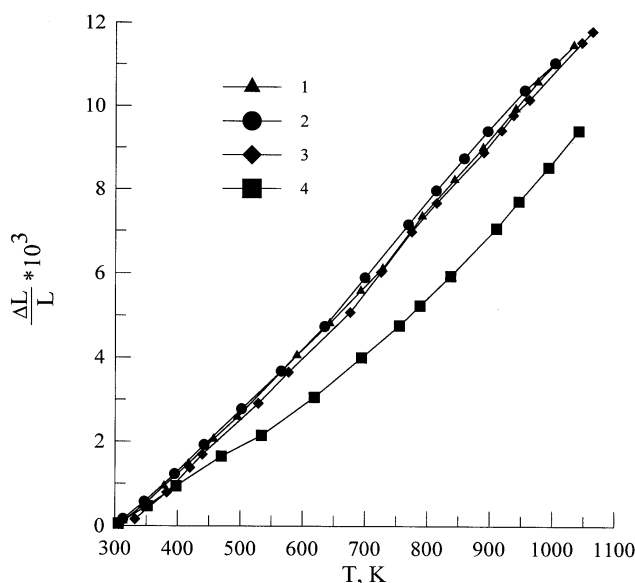


Fig.4. Dilatometric curves of BC0 (1), BLC1 (2), BLC2 (3), and BPC1 (4) in air.

The conductivity of BLC1 at temperatures above 500 K is slightly lower than that of BICUVOX.10; at lower temperatures, however, the conductivity values for the doped and undoped materials are close to each other (Fig.3). 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 poorer due to segregation of LaVO_4 as a second phase. BICUVOX doped with praseodymium had lower conductivity values than the lanthanum-doped analogue. The difference in conductivity between compositions is probably caused both by second-phase formation and a lower oxygen-vacancy concentration when Pr^{4+} cations are incorporated into the bismuth sublattice. The activation energy for electrical conductivity (E_a) was calculated using the standard Arrhenius model:

$$\sigma = \frac{A_0}{T} \cdot \exp\left[-\frac{E_a}{RT}\right] \quad [1]$$

where A_0 is the pre-exponential factor. Parameters for the regression model, described by Eq.(1), are given in Table 3. The activation energy values lie in the range of 45 – 58 kJ/mol at high temperatures (700 – 1050 K) and increase up to 62 – 69 kJ/mol in the low-temperature range 370 – 700 K. This increase in the activation energy at lower temperatures is associated with partial ordering of the oxygen sublattice [16].

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 e.m.f. method, vary from 0.90 to 0.99 in the temperature range 780 – 910 K (Table 2). These values are close to those previously reported in the literature (3,6). A higher temperature results in increasing electronic conductivity which is likely to take place via electron hopping between transition-metal cations ($\text{Cu}^{2+/1+}$ and $\text{V}^{5+/4+}$).

3.4. Thermal expansion

Table 2 lists the thermal expansion coefficients (TECs) calculated by fitting the dilatometric data. The dilatometric curves of the BICUVOX-based materials (Fig.4) exhibited considerable non-linearity, resulting in relatively high errors 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 similar, varying in a range of $(14.9 - 15.3) \times 10^{-6} \text{ K}^{-1}$ at temperatures from 300 to 700 K and $(17.7 - 18.0) \times 10^{-6} \text{ K}^{-1}$ from 730 to 1050 K. Doping by lanthanum results in slightly lower thermal expansion. The change in slope in the dilatometric curves near 700 K is, most probably, associated with the transition from partially ordered (so-called γ -phase) to completely disordered oxygen (16). This phase transition is accompanied by a decrease in the activation energy for ionic conduction (16). Such behaviour can be qualitatively explained in terms of the phenomenological theory of ionic transport (17) which states 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 found to be significantly lower than that of La-substituted BICUVOX ceramics, whereas at higher temperature, it increases to $16.1 \times 10^{-6} \text{ K}^{-1}$. It should be noted that doping with praseodymium also produces greater deviations from linearity in the dilatometric curves.

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 technique. Electrical properties of the oxides were shown to be essentially independent of the reaction precursors

and thermal history of the samples prior to sintering. The total electrical 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 lower than undoped BICUVOX.10, whereas transport properties of the two phases in the temperature range 370 – 450 K are similar. Impedance spectroscopy data suggest a uniform distribution of lanthanum in the grain bulk of $\text{Bi}_{1.90}\text{La}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$. 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 $\text{Bi}_{1.90}\text{Pr}_{0.10}\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$, however, secondary phases of LaVO_4 and BiVO_4 , respectively, have a deleterious effect on the electrical conductivity. Oxygen-ion transference numbers of compositions with moderate rare-earth dopant content ($x \leq 0.10$) were measured by a modified e.m.f. method to be 0.90 – 0.99 in a temperature range of 780 – 910 K, and to decrease with increasing temperature. Thermal expansion coefficients of $\text{Bi}_{2-x}\text{Ln}_x\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.5-\delta}$ are $(16.1 - 18.0) \times 10^{-6} \text{ K}^{-1}$ in the temperature range 730 – 1050 K. At lower temperatures, from 300 to 700 K, TECs of the La-substituted materials vary in the range $(14.9 - 15.3) \times 10^{-6} \text{ K}^{-1}$; doping with praseodymium leads to TEC values as low as $(10.5 \pm 0.5) \times 10^{-6} \text{ K}^{-1}$.

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REFERENCES

1. E.Pernot, M.Anne, M.Bacmann, P.Strobel, J.Fouletier, R.N.Vannier, G.Mairesse, F.Abraham and G.Nowogrocki, "Structure and conductivity of Cu and Ni-substituted $\text{Bi}_4\text{V}_2\text{O}_{11}$ compounds", *Solid State Ionics*, **70/71** 259-263 (1994).
2. R.N.Vannier, G.Mairesse, F.Abraham and G.Nowogrocki, "Double substitutions in $\text{Bi}_4\text{V}_2\text{O}_{11}$ ", *Solid State Ionics*, **70/71** 248-252 (1994).
3. J.C.Boivin, C.Pirovano, G.Nowogrocki, G.Mairesse, Ph.Labrune and G.Lagrange, "Electrode-electrolyte BIMEVOX system for moderate temperature oxygen separation", *Solid State Ionics*, **113-115** 639-651 (1998).
4. S.P.Simmer, D.Suarez-Sandoval, J.D.Mackenzie and B.Dunn, "Synthesis, densification and conductivity characteristics of BICUVOX oxygen-ion-conducting ceramics", *J. Am. Ceram. Soc.*, **80**, 2563-2568 (1997).
5. C.K.Lee, D.C.Sindair and A.R.West, "Stoichiometry and stability of bismuth vanadate, $\text{Bi}_4\text{V}_2\text{O}_{11}$, solid solutions", *Solid State Ionics*, **62**, 193-198 (1993).
6. A.A.Yaremchenko, V.V.Kharton, E.N.Naumovich and V.V.Samokhval, "Oxygen ionic and electronic conductivity of La-doped BIMEVOX", *Solid State Ionics*, **111**, 227-236 (1998).
7. M.F.Carolan, P.N.Dyer, S.M.Fine, A.Makitka, R.E.Richards and L.E.Schaffer, Method for manufacturing inorganic membranes by organometallic chemical vapor infiltration, US Patent 5,332,597 (1994).
8. G.Fafilek, "Voltammetry of BICUVOX.10 microsamples", *Solid State Ionics*, **113-115**, 623-629 (1998).
9. E.N.Naumovich, S.A.Skilkov, V.V.Kharton, A.A.Tonoyan and A.A.Vecher, "Solid oxide electrolytes in the system Bi_2O_3 -PbO- Y_2O_3 ", *Russian J. Electrochem.*, **30**, 642-645 (1994).
10. L.Navarro, F.Marques and J.Frade, "n-Type conductivity in gadolinia-doped ceria", *J. Electrochem. Soc.*, **144**, 267-273 (1997).
11. V.V.Kharton, A.V.Nikolaev, E.N.Naumovich and A.A.Vecher, "Oxygen ion transport and electrode properties of $\text{La}(\text{Sr})\text{MnO}_3$ ", *Solid State Ionics*, **81**, 201-209 (1995).
12. V.V.Kharton, E.N.Naumovich and V.V.Samokhval, "Formation and properties of reaction layers of cobaltite electrodes on bismuth oxide electrolytes", *Solid State Ionics*, **99**, 269-280 (1997).
13. R.T.Baker, B.Gharbage and F.M.B.Marques, "Processing and electrical conductivity of pure, Fe- and Cr-substituted $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_3$ ", *J. Eur. Ceram. Soc.*, **18**, 105-112 (1998).
14. A.A.Yaremchenko, V.V.Kharton, E.N.Naumovich, A.A.Tonoyan and V.V.Samokhval, "Oxygen ionic transport in Bi_2O_3 -based oxides: II. The Bi_2O_3 - ZrO_2 - Y_2O_3 and Bi_2O_3 - Nb_2O_5 - Ho_2O_3 solid solutions", *J. Solid State Electrochem.*, **2**, 308-314 (1998).
15. J.Rodriguez-Carvajal, "FULLPROF: a program for Rietveld refinement and pattern matching analysis, In: Satellite Meeting on Powder Diffraction", Abstracts of the XVth Conference of the International Union of Crystallography (Toulouse, 1990), p.127.
16. P.Kurek, P.Pongratz and M.W.Breiter, "Investigation of order-disorder transition in BICUVOX single crystals", *Solid State Ionics*, **113-115**, 615-621 (1998).
17. V.N.Chebodin, "Physical Chemistry of Solids" (Khimiya, Moscow, 1982).