

Structural and Thermal Stability of BIMEVOX Oxygen Semiconductors

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Abstract—The results on the structural and thermal stability of different modifications of solid solutions $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$ (BIFEVOX), where $x = 0.05\text{--}0.6$, and $\text{Bi}_4\text{V}_{2-x}\text{Cu}_{x/2}\text{Ti}_{x/2}\text{O}_{11-\delta}$ (BICUTIVOX), where $x = 0.025\text{--}0.50$, are shown. The stability is assessed by varying the thermodynamic parameters of the medium and also the time parameters with the use of modern methods, namely, the high-temperature X-ray diffraction analysis, the differential scanning calorimetry, and the dilatometry. The γ -modification of BIFEVOX is shown to be stable in a wide range of temperatures and oxygen partial pressures.

Keywords: BIMEVOX, oxygen-ionic conductors, thermal stability

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INTRODUCTION

The family of solid electrolytes with the general formula $\text{Bi}_4\text{V}_{2-x}\text{Me}_x\text{O}_{11-\delta}$ referred to as BIMEVOX demonstrated sufficiently high oxygen-ionic conductivity in the mid-temperature interval of 550–950 K. To be used as membranes in electrochemical devices, the materials should exhibit the structural and thermal stability in wide ranges of values of thermodynamic parameters and at the long exposures. The ranges of existence of $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$ and $\text{Bi}_4\text{V}_{2-x}\text{Cu}_{x/2}\text{Ti}_{x/2}\text{O}_{11-\delta}$ solid solutions and their structural and transport characteristics were studied and the peculiarities of phase transitions between polymorphous modifications were revealed [1, 2]. Samples of the BICUTIVOX family were crystallized in the γ -modification only after being quenched from a high temperature to room temperature. The region of existence of the γ -BIFEVOX modification was wider as regards both the concentration and the temperature. For the practical use, attention was focused on the behavior of these systems at long exposures to high temperatures in the vicinity of possible phase transition points.

EXPERIMENTAL

Compounds were synthesized according to the standard ceramics technology from the corresponding metal oxides in the temperature interval of 770–1070 K and also from liquid precursors. For the synthesis with liquid precursors, the solutions of bismuth, iron, and

copper nitrates were prepared in the required concentrations. Vanadium oxide was dissolved either in citric acid (in the mass ratio 1 : 3) to form vanadium citrate $2(\text{VO})\text{C}_6\text{H}_6\text{O}_7$ or in hydrogen peroxide. Titanium was introduced in the form of tetrabutoxy- or tetraethoxytitanium ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ or $\text{C}_8\text{H}_{20}\text{O}_4\text{Ti}$). For the chosen contents x of the substituted cation, the ratio of metal components in the reaction mixture was $\text{Bi} : \text{V} : \text{Me} = 4 : (2 - x) : x$. Solutions were mixed and, depending on the chosen synthesis procedure, either ammonia or polyvinyl alcohol (PVA) was added, then the mixture was heated and evaporated to afford the powder semi-product [1]. The final thermal treatment was carried out at temperatures of 873 and 1073 K. The phase composition of products was controlled by the XRD method (DRON-3 diffractometer, CuK_α emission, monochromator of pyrolytic graphite on reflected beam). The precision high-temperature XRD studies were carried out on a D8 ADVANCE diffractometer (CuK_α emission, β -filter, high temperature camera Anton Paar HTK 1200, position-sensitive detector VANTEC). The XRD analysis at the controlled partial oxygen pressure was carried out in the intervals of temperature of 770–1073 K and oxygen pressure $\log(P_{\text{O}_2} \times 10^{-5})$ from -0.667 to -18 [Pa] by means of a diffractometer DRON-3 and a high-temperature attachment UVD-2000 with the gas atmosphere sealed off from the environment. The precision control over the oxygen partial pressure in the reactor was provided automatically by a multifunctional regulator Zirconia318. Unit cell parameters were calculated

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Table 1. Regions of existence of structural modifications of $\text{Bi}_4\text{V}_{2-x}\text{Me}_x\text{O}_{11-\delta}$ solid solutions

Dopant	x for the corresponding modification			
	α (sp. gr. $C2/m$)	β (sp. gr. $Amam$)	γ (sp. gr. $I4/mmm$)	addition
Fe	0.05–0.15	0.175	0.25–0.50	0.55–0.7 – $Aba2$; 0.2 – mixture of $Amam$ and $I4/mmm$
CuTi	0.15	–	0.2–0.5	0.025–0.1 – $P-1$

using program packages TOPAS [3] and LMGP [4]. The particle sizes were determined by means of a particle size analyzer SALD-7101 Shimadzu. Dilatometric studies of sintered samples were carried out on a dilatometer DIL 402C Netzsch. Differential thermal analysis was accomplished in the temperature interval of 293–973 K by means of a thermoanalyzer STA 409 PC Luxx Netzsch. Aluminum oxide was used as the reference.

RESULTS AND DISCUSSION

Powders of solid solutions $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$ (BIFEVOX), where $x = 0.05\text{--}0.6$, and $\text{Bi}_4\text{V}_{2-x}\text{Cu}_{x/2}\text{Ti}_{x/2}\text{O}_{11-\delta}$ (BICUTIVOX), where $x = 0.025\text{--}0.50$, were synthesized. Using the XRD method, the boundaries of BIMEVOX homogeneity domains and the regions of existence of polymorphous modifications at room temperature were found. For the low content of the dopant metal (ME), the solid solutions were crystallized in monoclinic or orthor-

hombic modifications; with the increase in the dopant concentration, the tetragonal γ -modification was formed (Table 1). The average grain size in synthesized powders varied within 0.4–5 μm (the synthesis with liquid precursors) and 1–15 μm (the solid-phase synthesis).

The process of sintering of BIMEVOX ceramics was studied by dilatometric analysis in the non-isothermal mode. Briquettes for studying were prepared in the presence 5–10% PVA solution to prevent high brittleness. As the example, Figure 1 shows a typical dilatometric curve corresponding to the sintering process of $\text{Bi}_4\text{V}_{1.75}\text{Cu}_{0.125}\text{Ti}_{0.125}\text{O}_{11-\delta}$. The sintering proceeded in the same way for all samples irrespective of the solid solution composition and its polymorphous modification. For temperatures about 500 K, the binder was burned out and the linear dimensions of a sample decreased. With the further heating, only the thermal expansion of the sample was observed, which was accompanied by the $\alpha \rightarrow \beta$ or $\alpha \rightarrow \gamma$ phase transitions for solid solutions certified as the α -modi-

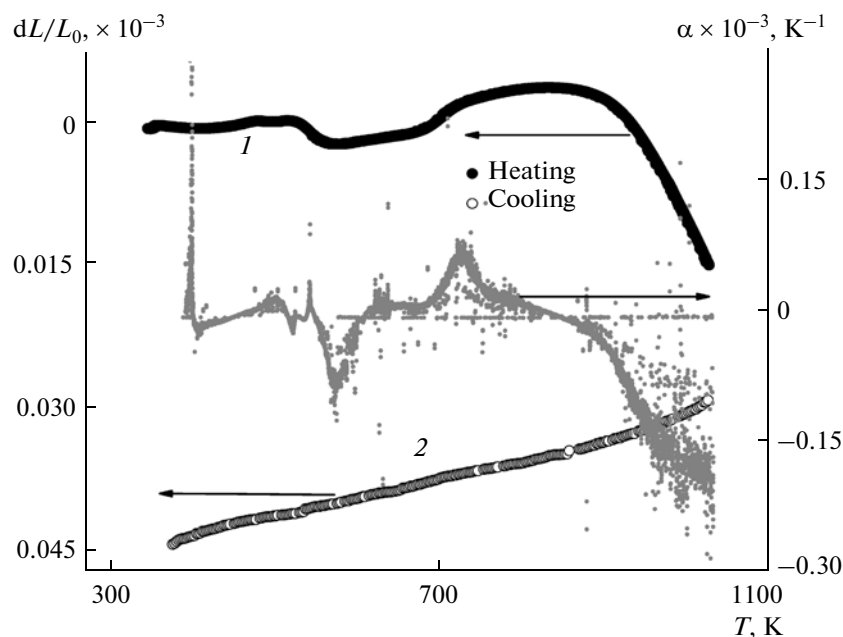
**Fig. 1.** Dilatometric curves of $\text{Bi}_4\text{V}_{1.75}\text{Cu}_{0.125}\text{Ti}_{0.125}\text{O}_{11-\delta}$ sintering: (1) heating, (2) cooling.

Table 2. Linear thermal expansion coefficients of BIMEVOX according to results of dilatometric studies

	x	Heating		Cooling	
		T, K	$\alpha \times 10^6, K^{-1}$	T, K	$\alpha \times 10^6, K^{-1}$
Fe	0.05	300–700	14.2	300–490	14.9
				550–700	14.6
	0.2	770–920	19.1	760–920	21.0
		300–590	15.1	300–540	14.8
	0.4	610–920	17.1	620–920	17.6
		300–690	15.3	300–710	15.4
0.5	710–920	17.0	750–920	17.9	
	300–620	14.5	300–710	14.8	
CuTi	0.075	800–920	16.7	770–920	17.2
		300–700	15.4	300–540	15.6
	0.1	750–790	16.1	620–740	15.1
		820–920	19.6	790–920	21.4
	0.125	300–700	15.8	300–510	15.9
				590–740	15.0
	0.25	800–920	19.9	770–920	20.8
		300–700	16.4	300–480	16.1
	0.25			540–700	15.0
				780–920	20.4
				760–920	21.1
				300–580	14.9
			640–790	15.1	
			820–920	22.3	

fication at room temperature. The most intense sintering began at 900 K, the maximum sintering rate was observed above 1000 K. Cooling after the sintering was illustrated by a typical dilatometric curve for BIMEVOX that demonstrated a break and a change in the slope of linear thermal expansion at phase transition temperatures for the corresponding compositions.

Based on the dilatometric data, the mean coefficients of linear thermal expansion (CLTE) of samples were calculated (Table 2). The most pronounced changes in the linear sizes were observed at the structural phase transition $\alpha \rightarrow \beta$. The highest CLTE values were typical of the high-temperature γ -modification with the low dopant concentrations and comparable with those of lanthanum–strontium cobaltites equal to $\sim 20 \times 10^{-6} K^{-1}$. Samples characterized at room temperature as the tetragonal γ -modification exhibited the phase transition $\gamma \rightarrow \gamma'$ of the order–disorder type accompanied by slight changes in CLTE.

The phase transition temperatures and the changes in structural parameters, which were observed during heating–cooling processes and at varying the oxygen

partial pressure, were assessed by the methods of high-temperature XRD, differential scanning calorimetry, and dilatometry on preliminarily sintered samples. For instance, a solid solution with the $Bi_4V_{1.9}Cu_{0.05}Ti_{0.05}O_{11-\delta}$ composition underwent two phase transitions on heating, which were accompanied by changes in the diffraction patterns in the corresponding temperature intervals and the appearance of bends in dilatometric and DSC curves. A similar picture was observed for the $\alpha \rightarrow \gamma$ phase transition of $Bi_4V_{1.925}Cu_{0.0375}Ti_{0.0375}O_{11-\delta}$ (Fig. 2). Table 3 shows the phase transition temperatures for BIMEVOX solid solutions determined by the dilatometric method.

Studies of the crystal structure of tetragonal $Bi_4V_{2-x}Fe_xO_{11-\delta}$ as a function of the temperature and the oxygen partial pressure showed that this modification was very stable in a sufficiently wide range of thermodynamic parameters. In certain cases (for example, for the $Bi_4Fe_{0.6}V_{1.4}O_{11-\delta}$ composition with the orthorhombic lattice), the temperature variations were shown to be accompanied by non-linear changes in parameter c at the monotonic variation of the other parameters including the unit cell volume. When heated to 840 K, the structure was retained and only the thermal expansion of a sample occurred, whereas in the temperature interval of 840–970 K, the structural changes were observed which were accompanied by the gradual convergence of parameters a and b . Moreover, these dependences were reproduced in the shape of heating–cooling cycles, which, together with the absence of transitions in the DSC and thermal expansion curves, pointed to the stability of BIMEVOX compositions (Fig. 3).

By varying the oxygen partial pressure, it was found that the structural transition from tetragonal to orthorhombic BIMEVOX modifications took place in media with low oxygen contents (for $\log(P_{O_2} \times 10^{-5}) = -18.0$ [Pa]) and the temperature above 770 K. However, throughout the studied intervals of the temperature $298 \leq T \leq 1073$ K and the oxygen partial pressures $-18 \leq \log(P_{O_2} \times 10^{-5}) \leq 0.667$ [Pa], no destruction of samples was observed.

To assess the structural and thermal and stability of BIMEVOX in air for long exposure times, the samples were annealed sequentially at temperatures 723, 823, 923, 973, 1023, 1083 K in the direct and reverse order with the exposure for two weeks at each temperature. For all BICUTIVOX compositions, the changes in the cell symmetry and the presence of phase transitions were observed in durable heating–cooling cycles. Moreover, certain compositions were partially destroyed to afford impurities. For example, in the $Bi_4V_{1.95}Cu_{0.025}Ti_{0.025}O_{10.95}$ composition, the $BiVO_4$ (~4%) and $Bi_{3.5}V_{1.2}O_{8.25}$ (~1%) impurities appeared after 2-week annealing at 823 K. The mixture was completely transformed into the BICUTIVOX solid solution at subsequent annealing at 923 K. As the tem-

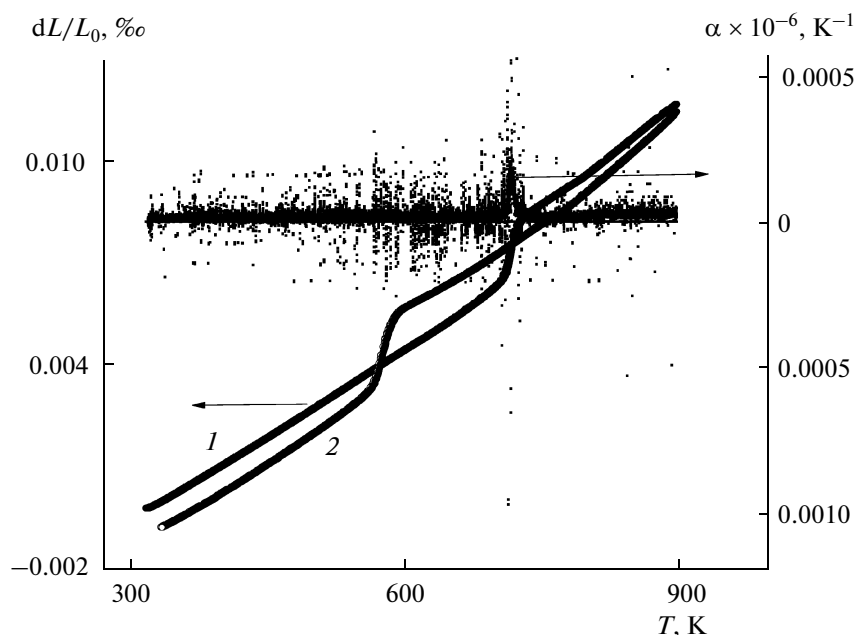


Fig. 2. Dilatometric curves of sintering of $\text{Bi}_4\text{V}_{1.925}\text{Cu}_{0.0375}\text{Ti}_{0.0375}\text{O}_{11-\delta}$: (1) heating, (2) cooling.

perature increased further to 1083 K, the monoclinic $\text{Bi}_4\text{V}_{1.95}\text{Cu}_{0.025}\text{Ti}_{0.025}\text{O}_{10.95}$ modification transformed to tetragonal, whereas lowering down of temperature to 1023 K transformed the high-temperature γ -modification back to the monoclinic modification with the lower symmetry.

The BIFEVOX solid solutions behaved differently. When samples were exposed to 823 K (2-week annealing), the impurities with the BiVO_4 (~4%) and

$\text{Bi}_{3.5}\text{V}_{1.2}\text{O}_{8.25}$ (~1%) composition appeared in $\text{Bi}_4\text{V}_{1.95}\text{Fe}_{0.05}\text{O}_{10.95}$ and $\text{Bi}_4\text{V}_{1.9}\text{Fe}_{0.1}\text{O}_{10.9}$ samples (identified as the α -modification after the synthesis) in addition to the main BIMEVOX solid solution. The mixture transformed completely back to BIFEVOX after its exposure at 923 K for both compositions.

For $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$ samples with $x = 0.3$ and 0.4 certified as the γ -modification and also for a sample with $x = 0.6$ and the unit cell with the orthorhombic

Table 3. Temperatures of phase transitions of $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$ and $\text{Bi}_4\text{V}_{2-x}\text{Cu}_{x/2}\text{Ti}_{x/2}\text{O}_{11-\delta}$ determined by dilatometry

Composition, Me	Modification at room temperature according to XRD	Composition, x	Phase transition temperature, K			
			$\alpha \rightarrow \beta$	$\beta \rightarrow \gamma$	$\gamma \rightarrow \gamma'$	
Fe	α (sp. gr. $C2/m$)	0.05	651	820	—	
		0.1	515	784	—	
		0.125	481	780	—	
	β (sp. gr. $Amam$)	0.175	—	763	—	
		0.2	—	764	—	
	γ (sp. gr. $I4/mmm$)	0.3	—	—	760	
		0.4	—	—	850	
CuTi	α (sp. gr. $P-1$)	0.6	—	—	887	
		0.025	669	818	—	
		0.05	671	811	—	
		0.075	655	799	—	
		0.1	648	773	—	
	α (sp. gr. $C2/m$)	0.125	617	765	—	
		β (sp. gr. $Amam$)	0.2	—	—	—
		γ (sp. gr. $I4/mmm$)	0.25	—	—	—

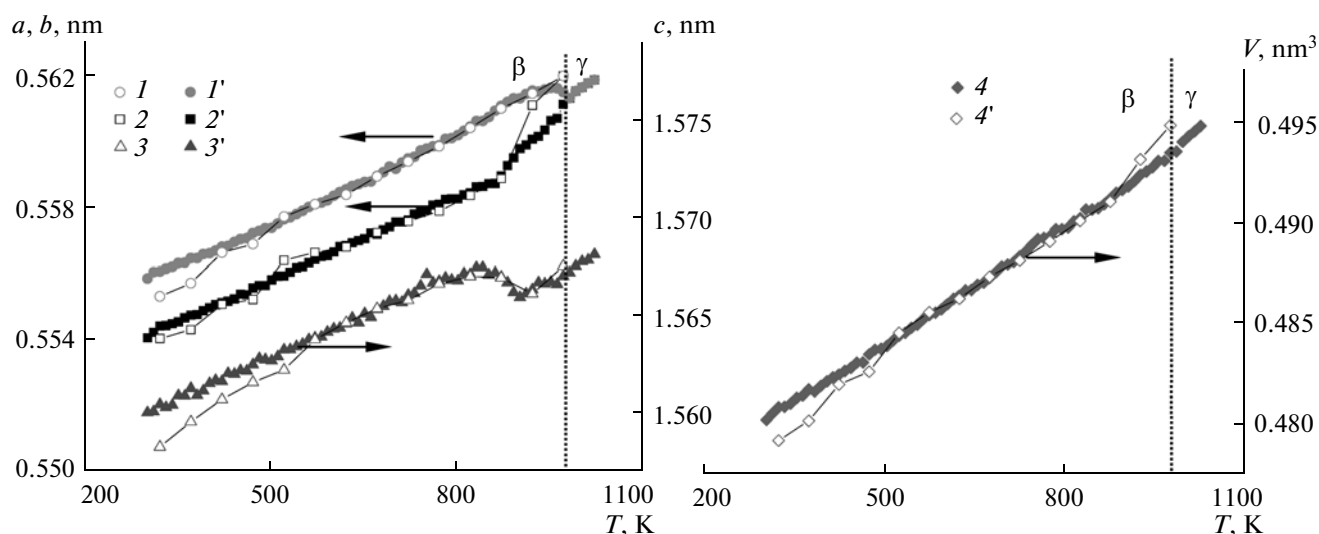


Fig. 3. Unit cell parameters as a function of temperature for $\text{Bi}_4\text{V}_{1.4}\text{Fe}_{0.6}\text{O}_{11-\delta}$: (I, I') parameter b ; ($2, 2'$) parameter a ; ($3, 3'$) parameter c ; ($4, 4'$) V unit cell volume. Curves $I-4$ pertain to the cooling process, curves $I'-4'$ pertain to heating.

symmetry, neither structural changes nor additional phases were observed throughout the temperature region. This suggests that this series of solid solutions remained stable throughout thermocyclic tests.

Thus, comparing the parameters of structural and thermal stability for two series of solid solutions, it must be admitted that $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$ solid solutions ($x = 0.3-0.6$) proved to be more suitable materials for electrochemical devices as regards their use in the long-term cycles with varied parameters of the medium.

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