

# Synthesis, Region of Existence, Structural Characteristics, and Conductivity of BI(CR, FE)VOX Solid Solutions<sup>1</sup>

E. V. Velichko<sup>a</sup>, Z. A. Mikhailovskaya<sup>a</sup>, M. V. Morozova<sup>a</sup>, E. S. Buyanova<sup>a, z</sup>,  
Yu. V. Emel'yanova<sup>a</sup>, S. A. Petrova<sup>b</sup>, and V. M. Zhukovskii<sup>a</sup>

<sup>a</sup>Ural State University, Yekaterinburg, Russia

<sup>b</sup>Institute of Metallurgy, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia

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**Abstract**—The results of our studies of solid solutions of the general composition  $\text{Bi}_4\text{V}_{2-x}\text{Fe}_{x/2}\text{Cr}_{x/2}\text{O}_{11-\delta}$  are presented. The crystal-chemical parameters of different polymorphic modifications of BIMEVOX were determined. The particle size distribution was determined by laser diffraction and optical microscopy. The surface of sintered preforms was studied by scanning electron microscopy. The conductivity of sintered polycrystalline samples as a function of temperature and composition was studied by impedance spectroscopy. The conductivity depends on the procedure for the synthesis of solid solutions. The most promising compositions were revealed.

**Keywords:** BIMEVOX, oxygen ion conductors, impedance spectroscopy

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## INTRODUCTION

The promising oxygen ion conductors include solid substitution solutions based on bismuth vanadate  $\text{Bi}_4\text{V}_2\text{O}_{11}$  that form the BIMEVOX family [1]. Bismuth vanadate can be considered a member of so-called Aurivillius phases (APs)  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ , where  $n = 1$ . The crystal structure of the first member of this series,  $\gamma\text{-Bi}_2\text{WO}_6$ , contains an octahedral layer of  $[\text{WO}_4]^{2-}$  anions. In view of the similarity of the crystal structures of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  ( $\text{Bi}_2\text{VO}_{5.5}$ ) and  $\gamma\text{-Bi}_2\text{WO}_6$ , bismuth vanadate can be recorded as  $[\text{Bi}_2\text{O}_2]^{2+}[\text{VO}_{3.5}\square_{0.5}]^{2-}$ , where  $\square$  is the oxygen vacancy. The  $(\text{VO}_{3.5}\square_{0.5})^{2-}$  layers are divided into rows of tetrahedra and oxygen-deficient octahedra. The oxygen vacancies involved in ionic conductivity lie around the vanadium atoms in the octahedra in the central part. This compound is characterized by high oxygen ion conductivity (of the order of  $10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$  at 773 K) and polymorphism [1, 2]. The sequence of reversible phase transitions for  $\text{Bi}_4\text{V}_2\text{O}_{11}$  can be represented as  $\alpha \xleftarrow{720 \text{ K}} \beta \xleftarrow{840 \text{ K}} \gamma \xleftarrow{1150 \text{ K}} \gamma' \xleftarrow{1160 \text{ K}} \text{liquid}$  [3]. All modifications are characterized by the alternation of  $(\text{Bi}_2\text{O}_2)_n^{2n+}$  and  $[\text{VO}_{3.5}\square_{0.5}]^{2-}$  layers; the differences in polymorphism are determined only by the variants of the vanadate layer ordering. In  $\text{Bi}_4\text{V}_2\text{O}_{11}$

solid solutions, the regions of existence of structural modifications vary with the dopant concentration and nature. The best conductivity is characteristic of the high-temperature  $\gamma$  modification of BIMEVOX, having the greatest disordering in the oxygen sublattice. The  $\gamma$  form is stabilized at room temperature by replacing some part of vanadium with different elements (e.g., ME = Ge, Co, Cu, Ti, Ni, Zr, etc. [4–7]). At  $\sim 570 \text{ K}$  several compositions have ion conductivity that is two orders of magnitude higher than that of electrolytes based on zirconium dioxide [7]. Studies of iron-substituted (BIFEVOX) solid solutions were reported in [8–10]. The structural parameters and regions of existence of the structural modifications of  $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$  (BIFEVOX) solid solutions were determined in [9]. Solid solutions in the monoclinic  $\alpha$  modification formed at low iron contents  $x = 0.05\text{--}0.1$  (space group  $C2/m$ ). The compositions with  $x = 0.125$  and  $0.15$  are mixtures of the  $\alpha$  and  $\beta$  forms. At  $0.2 < x < 0.7$  a  $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-\delta}$  solid solution with a structure of the  $\gamma$  modification of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  formed (space group  $I4/mmm$ ). The region of existence of the  $\beta$  form in this system near the composition with  $x = 0.175$  was reported to be very narrow.  $\text{Bi}_4\text{V}_{2-x}\text{Cr}_x\text{O}_{11-\delta}$  solid solutions ( $x \leq 0.5$ ) formed when vanadium was replaced with chromium at the oxidation level +3 [1]. At room temperature, the structural type of all solid solutions is that of the orthorhombic  $\alpha$  modification but changes to that of the tetragonal  $\gamma$  form on heating. As noted in [11], the  $\alpha$  form is stabilized after the

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<sup>z</sup> Corresponding author: Elena.Buyanova@usu.ru (E.S. Buyanova).

introduction of  $\text{Cr}^{3+}$  because this ion has a regular octahedral environment of oxygen ions and a strong  $\text{Cr}^{3+}-\text{O}^{2-}$  covalent bond. At higher  $\text{Cr}^{3+}$  contents, the content of vanadium with a tetragonal environment increases and defects are blocked in the structure. A comparison of the structural and conducting characteristics of  $\text{Bi}_2(\text{V}_{0.95}\text{TM}_{0.05})\text{O}_{5.5+\delta}$ , where TMs are the transition metals, was presented in a recent paper [12]. According to the literature data, the chromium-substituted composition crystallizes in the orthorhombic  $\alpha$  or  $\beta$  modification at room temperature depending on the cooling rate during the synthesis. The oxygen transfer number measurements and impedance measurements of conductivity in a number of studies proved the predominantly oxygen ion transport in BIMEVOX compounds, where ME are transition metals. The BICUVOX solid solutions doped with rare-earth metal (La, Pr) were studied in the temperature range 370–1070 K [13]. The oxygen transfer numbers measured by the EMF method were 0.9–0.99 at 780–910 K. Impedance measurements confirmed that the conductivity of  $\text{Bi}_4\text{V}_{2-2x}\text{M}_{2x}\text{O}_{11-2x}$  solid solutions (where M = rare-earth metal) was purely (or basically) ionic. The oxygen transfer number was reported to be  $t_{\text{O}^{2-}} = 0.98$  for the  $\text{Bi}_2(\text{V}_{0.95}\text{Cr}_{0.05})\text{O}_{5.5+\delta}$  composition at 973 K [12] and 0.97 for  $\text{Bi}_2(\text{V}_{0.90}\text{Cu}_{0.1})\text{O}_{5.5+\delta}$  at 923 K in air [14]. This work presents a detailed study of solid solutions with vanadium replaced by iron and chromium (BICRFEVOX family).

## EXPERIMENTAL

The  $\text{Bi}_4\text{V}_{2-x}\text{Fe}_{x/2}\text{Cr}_{x/2}\text{O}_{11-\delta}$  solid solutions were synthesized by the standard ceramic procedure at 773–1073 K at a step of 50 K. As the starting compounds, we used bismuth oxide  $\text{Bi}_2\text{O}_3$  (ultra high grade), vanadium oxide  $\text{V}_2\text{O}_5$  (ultra high grade), iron oxide  $\text{Fe}_2\text{O}_3$  (ultra high grade), and chromium oxide  $\text{Cr}_2\text{O}_3$  (ultra high grade). The substances were preliminarily calcinated in a furnace at 873 K to remove the traces of moisture. The samples were cooled together with the furnace after each stage and thoroughly ground in an agate mortar with an ethanol addition as a homogenizer.

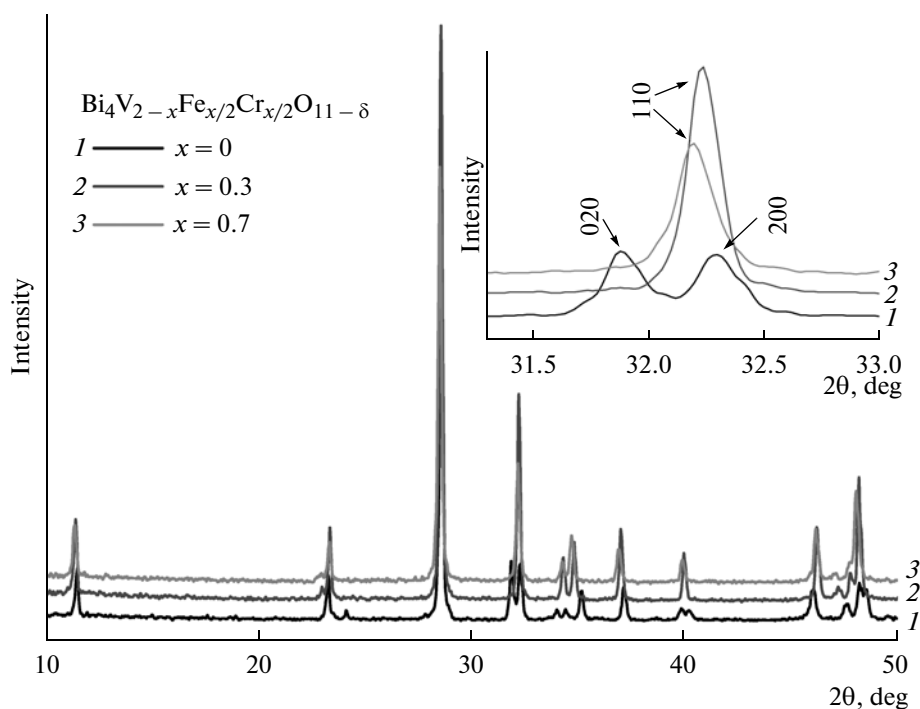
For pyrolysis of polymeric salt compositions (PSCs), we chose bismuth oxide  $\text{Bi}_2\text{O}_3$ , vanadium oxide  $\text{V}_2\text{O}_5$ , iron nitrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , chromium nitrate  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , concentrated nitric acid, hydrogen peroxide, and polyvinyl alcohol. Bismuth oxide, iron nitrate, and chromium nitrate were dissolved in nitric acid. Vanadium oxide was dissolved in nitric acid and hydrogen peroxide. The resulting solutions were mixed and polyvinyl alcohol was added. The resulting mixture was evaporated with further

thermal decomposition by pyrolysis. The final thermal treatment was performed for 6 h at 923–1073 K.

The phase composition of the intermediate and final products was determined by X-ray diffractometry (DRON-3 diffractometer,  $\text{CuK}_\alpha$  radiation, pyrolytic graphite monochromator on a reflected beam). The unit cell parameters were calculated and the crystal structure refined with TOPAS [15] and LMGP [16] program packages. The powder particle sizes were determined by laser diffraction (SALD-7101 Shimadzu dispersity laser analyzer). The surface of the sintered preforms was studied by electron microscopy (VEGA/TESCAN scanning electron microscope). The density of the sintered preforms was calculated from the experimental bottle and bulk densities of ceramics. The bulk density was determined by hydrostatic weighing. The conductivity of the samples was studied by impedance spectroscopy (Elins Z-2000, Elins Z-3000, and Elins-Z-350M) at 1073–473 K.

## RESULTS AND DISCUSSION

The solid solutions of the general composition  $\text{Bi}_4\text{V}_{2-x}\text{Cr}_{x/2}\text{Fe}_{x/2}\text{O}_{11-\delta}$ , where  $x = 0.1-1.5$ , were synthesized by the standard ceramic procedure or pyrolysis (PSC method). The boundaries of the homogeneity regions and the existence regions (whose boundaries are independent of the synthetic procedure) of the structural modifications of the resulting solid solutions were determined using the XRD data. The samples with the dopant content  $x = 0.1$  synthesized by different procedures were orthorhombic (space group *Amam*). This agrees with the literature data on BIMEVOX with only one of the transition metals substituted [9, 11, 12]. The samples with  $0.2 \leq x \leq 0.7$  were attributed to the tetragonal crystal system (space group *I4/mmm*), which fully corresponds to the BIFEVOX family in the structural parameters and length of this region [9]. The tetragonal  $\gamma$  modification was also found at higher  $x = 0.8-1.1$ , but then it exists together with various admixtures ( $\text{BiCrO}_3$  and a Cr-containing compound isostructural to  $\text{Bi}_{13}\text{Mo}_4\text{VO}_{34}$ ). At  $x > 1.1$ , the solid BICRFEVOX residue does not exist; the X-ray diffraction patterns showed the reflections of other phases. The boundary of homogeneity of BICRFEVOX, therefore, lies at  $x \leq 0.7$ . Figure 1 presents the X-ray diffraction patterns for several BICRFEVOX compositions as an example to demonstrate the structural features of modifications and the possibilities for the formation of solid solutions. The X-ray profiles for the orthorhombic (space group *Amam*) and tetragonal (space group *I4/mmm*) modifications are identical, the form with lower symmetry showing the splitting of several characteristic reflections. For example, the (110) reflection is transformed into a doublet consisting of the (020) and (200) lines in the range of angles around  $32^\circ$  for



**Fig. 1.** X-ray diffraction patterns of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  and  $\text{Bi}_4\text{V}_{2-x}\text{Cr}_{x/2}\text{Fe}_{x/2}\text{O}_{11-\delta}$  ( $x = 0.3, 0.7$ ). Insert: one of the characteristic  $2\theta$  ranges.

the  $\beta$  phase. The lattice parameters of the resulting solid solutions are presented in Table 1. Note that the insignificant change in the  $a$  parameter compared with  $c$  in the region of the existence of the tetragonal form is characteristic of the BIMEVOX family of compounds, e.g., with iron, chromium [8–10], or germanium [4] single dopants or (Ce,Ti) double dopants in the vanadium sublattice [5] or (Fe,La) double dopants [17] in other sublattices. This is determined by the layered structure of BIMEVOX, in particular, by the rigid framework of the bismuth–oxygen layer  $(\text{Bi}_2\text{O}_2)_n^{2n+}$ , whose effect on the  $a$  and  $b$  parameters exceeds that of the layer of vanadium–oxygen polyhedra.

The grain sizes of powder samples obtained by different procedures were determined by laser diffraction. For samples obtained by the PSC procedure, the grain size was found to be 5–10  $\mu\text{m}$ , which is an order of magnitude lower than for the sample obtained by solid-state synthesis (30–50  $\mu\text{m}$ ).

The surface of the sintered preforms was studied by scanning electron microscopy. Figure 2 shows the typical micrograph of the surface with fused agglomerates of particles whose average size is 25–40  $\mu\text{m}$ . We can see pores and cracks, indicating that the surface is nonuniform. The density of BIMEVOX preforms sintered at 970–1020 K for 2–4 h is up to 83% irrespective of the composition and synthetic procedure. Earlier impedance spectroscopy studies [18, 19] showed

that the density of BIMEVOX preforms was not critical to the total conductivity of the samples.

The conductivity of solid solutions was studied by impedance spectroscopy at 473–1073 K. Measurements were performed by the double-contact method using platinum electrodes on preliminarily sintered preforms. Figure 3 shows the typical impedance plots for one sample at different temperatures. The form of

**Table 1.** Crystal data for  $\text{Bi}_4\text{V}_{2-x}\text{Cr}_{x/2}\text{Fe}_{x/2}\text{O}_{11-\delta}$  samples

$x$	$a$ $\pm 0.0002$ nm	$b$ $\pm 0.0005$ nm	$c$ $\pm 0.0005$ nm	$V$ $\pm 0.0007$ nm <sup>3</sup>
0.1	5.539	5.592	15.423	0.47772
0.2	3.924	3.924	15.421	0.23747
0.3	3.927	3.927	15.459	0.23843
0.4	3.926	3.926	15.466	0.23848
0.5	3.927	3.927	15.479	0.23857
0.6	3.929	3.929	15.495	0.23938
0.7	3.931	3.931	15.514	0.23977

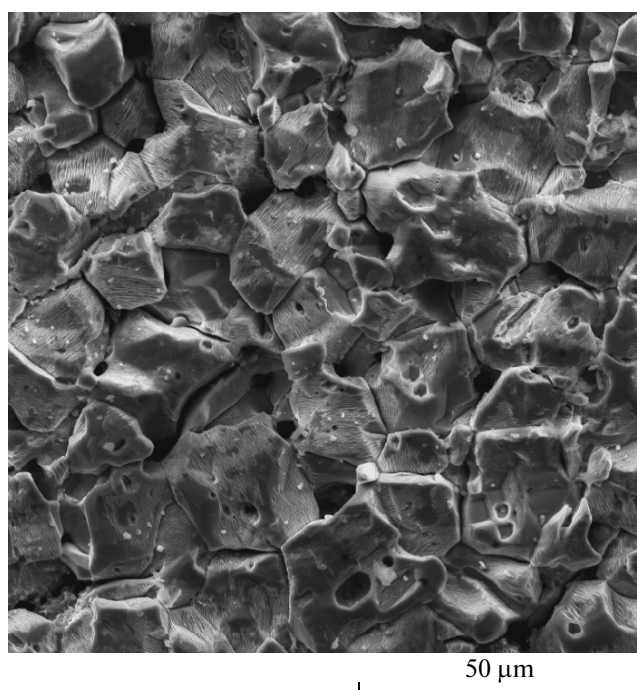


Fig. 2. Micrograph of the surface of a sintered preform from the  $\text{Bi}_4\text{Cr}_{0.15}\text{Fe}_{0.15}\text{V}_{1.7}\text{O}_{11-\delta}$  sample.

the dependence changes with temperature. At relatively low temperatures (623 K), the impedance plot consists of several combined semicircles. The low-fre-

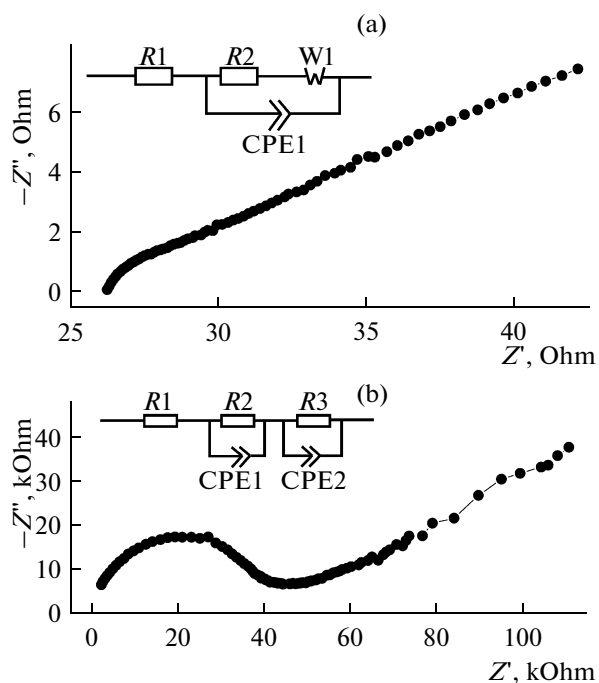
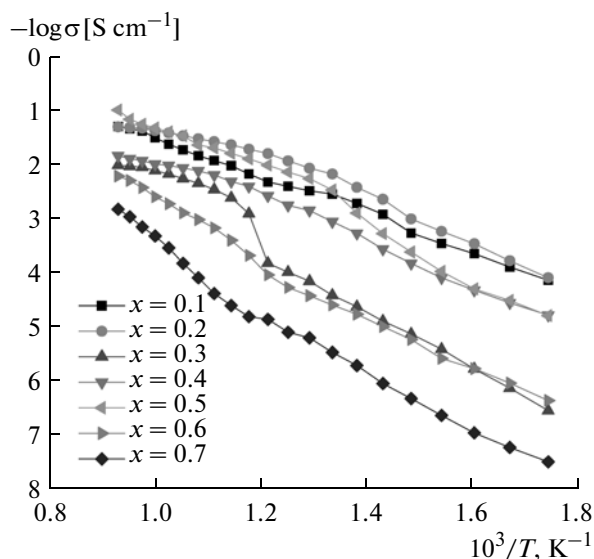


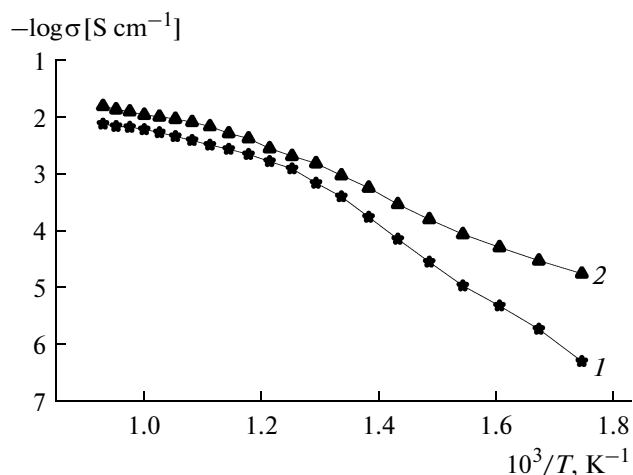
Fig. 3. Impedance plot of the  $\text{Bi}_4\text{V}_{1.6}\text{Fe}_{0.2}\text{Cr}_{0.2}\text{O}_{11-\delta}$  sample at (a) 1023 K and (b) 623 K.

quency part of the curve becomes smoother at lower temperatures. The equivalent circuits of the cells corresponding to processes in definite temperature ranges were chosen using Zview software (version 2.6b, Scribner Associates, Inc.). The point at which the semicircle intersects the  $Z'$  axis corresponds to volume conductivity extrapolated to large frequencies at low temperatures. The intersection of this circle with the abscissa in the low-frequency range corresponds to conductivity at grain boundaries. These components are described by the resistance  $R1$  and so-called Voigt element (which is parallel to  $R2$  and  $CPE1$ ), respectively. The low-frequency part of the plot, described here by the second Voigt element consisting of  $R3$  and  $CPE2$  of the equivalent circuit, corresponds to the processes on the electrode/electrolyte boundary and in electrodes. At higher temperatures, the circles are degenerated, making it impossible to separate the volume and grain boundary components. The total conductivity of the sample then corresponds to the resistance  $R1$  of the equivalent circuit. The impedance data were used to construct the dependences of the total conductivity of the samples on the reciprocal temperature. The data are presented in Fig. 4. The curves were found to be typical for the BIMEVOX family; the conductivity increased to certain values of  $x$  (here,  $x = 0.2$ ) and decreased markedly at higher concentrations of the replacing component. There is still no consensus of opinion on reasons for this effect but defects are considered to clusterize at certain dopant contents, decreasing



**Fig. 4.** Temperature dependence of conductivity for the samples of the general composition  $\text{Bi}_4\text{V}_{2-x}\text{Cr}_{x/2}\text{Fe}_{x/2}\text{O}_{11-\delta}$ .

the total conductivity [20]. The main electrophysical characteristics of the  $\text{Bi}_4\text{V}_{2-x}\text{Fe}_{x/2}\text{Cr}_{x/2}\text{O}_{11-\delta}$  solid solutions are given in Table 2. The temperature dependences of conductivity of samples with the same composition obtained by different methods were compared. As can be seen in Fig. 5, the samples synthesized by the PSC method were better conductors than those obtained by solid-state synthesis. This was explained [9] by the formation of denser ceramics for samples obtained by the PSC procedure because of smaller grains.



**Fig. 5.** Temperature dependence of conductivity for  $\text{Bi}_4\text{V}_{1.4}\text{Cr}_{0.2}\text{Fe}_{x/2}\text{O}_{11-\delta}$  samples obtained by (1) solid-state synthesis and (2) PSC pyrolysis.

To summarize, we have studied the homogeneity region of the BICRFEVOX solid solutions; the particle size distribution of the powder samples; and the samples with the highest conductivity, which was measured by impedance spectroscopy after sintering. The samples obtained by the PSC procedure were shown to be the best conductors.

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**Table 2.** Electrophysical characteristics of  $\text{Bi}_4\text{V}_{2-x}\text{Fe}_{x/2}\text{Cr}_{x/2}\text{O}_{11-\delta}$  solid solutions

$x$	$T$ , K	$E_{\text{act}}$ , eV	$-\log \sigma$ [ $\text{S cm}^{-1}$ ]	
			$T = 723$ K	$T = 1023$ K
0.1	1073–673	0.69	2.29	1.34
	673–473	0.79		
0.2	1073–473	0.69	1.76	1.30
	948–473	1.03		
0.3	1073–948	0.68	3.78	2.01
	948–473	1.03		
0.4	1073–473	0.77	2.54	1.89
0.5		0.96	1.98	1.22
0.6		1.05	4.00	2.39
0.7		1.15	4.82	3.12

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