Highconducting oxide ceramics bimevox: Synthesis, structure, and properties

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ARTICLE INFO

ABSTRACT

Materials on the basis of BIMEVOX compounds which are stable within wide concentration and temperature regions have been obtained. Refinement of crystal structure of different BIMEVOX modifications obtained at different temperatures and partial oxygen pressures has been carried out. The most promising solid solutions have been identified according to total conductivity value as well as to linearity of conductivity dependence on temperature and independence of that on partial oxygen pressure.

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1. Introduction

Solid solutions based on bismuth vanadate $Bi_4V_2O_{11}$, where vanadium is partly substituted by another cation (ME), give BIMEVOX family which is characterized by high oxygen-ion conductivity at moderate temperatures. The largest disorder of the oxygen sublattice is typical for high-temperature γ-modification when all oxygen atoms in the vanadium octahedral are involved into the diffusion processes. It leads to the highest conduction value and the lowest activation energy [1,2]. To use BIMEVOX family compounds as oxygen conductors it is necessary to obtain ceramics in a stable high-conducting modification, with small grain sizes and proper thermo-mechanical properties. In this article several BIMEVOXes (Me = Fe, Cr, Nb) were synthesized using different methods and studied by the use of dilatometry, high-temperature X-Ray measurements, scanning electron microscope in conjunction with their electrical properties investigated by impedance spectroscopy.

2. Experimental

Solid solutions of the general formula $Bi_4V_{2-x}Me_xO_{11-\delta}$, (Me = Fe, Cr, Nb) were synthesized by means of hydrochemical, citrate-nitrate, mechanochemical, pyrolysis of polymeric-salt compositions methods. The following concentration regions were chosen for the synthesis: $x = 0$–0.7 (Fe), $x = 0$–0.9 (Nb, (Cr,Fe), Cr). Bismuth and metals (Me) nitrates, vanadium oxide, hydrogen peroxide, citric acid, ammonia, nitric acid, polyvinyl alcohol were used as initial reagents. Solutions of salts of metals used were mixed with ammonia or polyvinyl alcohol. Final thermal treatment of initial powders included annealing at 770 and 970 K during a few hours. Composition and phase formation processes were controlled by means of X-Ray diffraction method (XRD) using CuK_α-radiation, monochromator of pyrolytic carbon on reflected beam. High-temperature XRD measurements were fulfilled with D8 ADVANCE diffractometer. Program packages TOPAS [3] and LMGP [4] were used for cell parameters calculations and crystal structure refinement. Dilatometric investigations were made with DIL 402C Netzsch dilatometer. Electrical conductivity was measured by means of impedance spectroscopy method (Elins Z-2000, Elins Z-350 M imped-ance meters) within 1070–470 K temperature region. Sample prepara-tion for impedance spectroscopy measurements involved compacting and annealing polycrystalline briquettes at 1073–1123 K for 2–4 h in air. To achieve better contact between platinum electrode and BIMEVOX electrolyte both face planes of briquettes were covered with fine-crystalline platinum using thermal decomposition of $(NH_4)_2PtCl_6$. Micrographs of polished and etched by nitric acid briquettes were made by means of VEGA/TESCAN scanning electron microscope.

3. Results

According to XRD results the single phase solid solutions are formed within chosen concentration regions except Cr-containing samples. Table 1 shows regions of different structural modifications existence for chosen dopant metals. At rather low values of x in $Bi_4V_{2x}Nb_xO_{11}$ α-phase is formed with either monoclinic (space group $C2/m$) or orthorhombic (space group $Aba2$) structure depending on method of synthesis applied. Orthorhombic β-phase is obtained only

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Table 1
Regions of structural modifications existence of BIMEVOX solid solutions.

| Dopant	α (space group Aba2)	α (space group C2/m)	β (space group Amam)	γ (space group I4/mmm)
Fe	0.55–0.7	0.05–0.15	0.175	0.20–0.50
Nb	0.05–0.15	0.05–0.15	–	0.2–0.9
Cr	–	–	0.1–0.3	0.4
CrFe	–	–	0.1	0.2–0.7

Table 2
Structural parameters of $Bi_4V_{1.8}Fe_{0.2}O_{10.8}$. Sp.gr. $Aba2$ $a = 5.5676(1)$ Å, $b = 15.4087$ (3) Å, $c = 5.5497$ (1) Å, $V = 476.108$ (17) Å^3.

Atom	Factor	X	Y	Z	Occupancy	B_{iso}
Bi	8	0.5068	0.1688	0.0	1.12	1.01
V/Fe	4	0.0670	0.0	−0.0446	1.01	0.88
O1	8	0.254	0.256	0.254	0.99	1.42
O2	8	0.276	0.512	0.364	1.02	1.42
O3	8	−0.085	−0.103	0.106	0.98	1.42
GOF = 2.95; Rwp = 6.46, Rp = 4.87; R_{Bragg} = 2.04						

for BIFEVOX solid solutions at $x = 0.175$. High dopant concentrations usually lead to formation of the high-temperature tetragonal γ-modification of $Bi_4V_2O_{11}$ (space group $I4/mmm$) up to the high border of solid solutions existence [5]. The exception is BIFEVOX series, for which above ca. $x = 0.5$ orthorhombic symmetry appears again as a result of a structure resembling that observed for lower x-value compositions. Similar results were obtained earlier for BIMGVOX samples [6]. Crystal structure refinement of different BIMEVOX polymorphic modifications was made by means of Rietveld full profile method. As an example Table 2 shows structure parameters of $Bi_4V_{1.8}Fe_{0.2}O_{10.8}$ synthesized by mechanochemical method.

Average grain size of BIMEVOX solid solutions obtained by liquid precursors methods varies in rather wide region from 0.3 to 10 µm although the distribution maximum is in general equal to 1–3 µm. Photomicrography of sintered briquette surface of the sample with tetragonal structure is shown in Fig. 1. Grain borders and non-uniformity of grain sizes are well seen. Perhaps this is due to crystallites growth anisotropy.
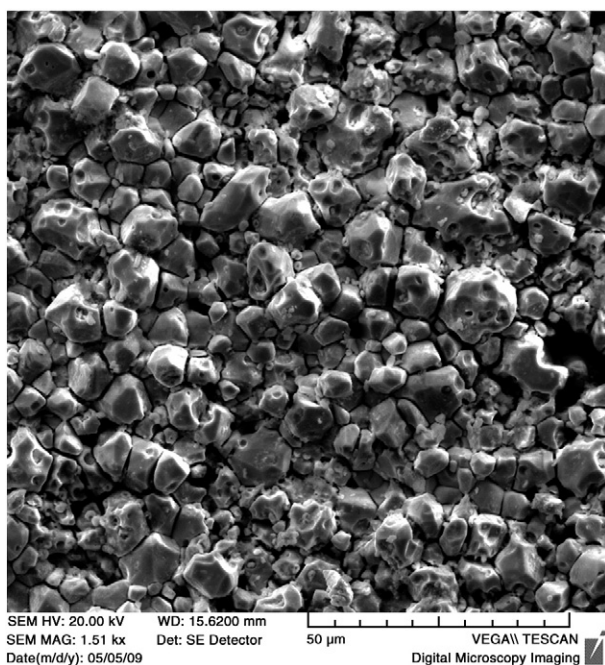
Fig. 1. Photomicrography of $Bi_4V_{1.3}Nb_{0.7}O_{11}$.

To determine temperature borders of polymorph transitions high-temperature X-Ray and dilatometric investigations within 298–1023 K temperature region have been carried out. Effects corresponding to phase transitions are observed on the linear thermal expansion and thermal expansion physical factor curves. Phase structural transition of type I: $C2/m \rightarrow Amam$ $(Aba2) \rightarrow I4/mmm$ (ME = Fe; Nb) or $Amam$ $(Aba2) \rightarrow I4/mmm$ (ME = Cr; (Cr,Fe)) has been found in the temperature region of 473–843 K for BIMEVOX solutions with low dopant concentration. Under conditions of large x content when high-temperature modification is stabilized within the whole concentration range no phase transitions in the temperature region investigated take place. X-Ray data are in a good agreement with dilatometric investigations. Complex investigation of tetragonal BIMEVOX (Me = Fe, Nb) crystal structure upon temperature and oxygen partial pressure revealed considerable stability of BIFEVOX and BINBVOX within a wide range of thermodynamical parameters. Elementary cell parameters of $Bi_4V_{1.6-}Nb_{0.6}O_{11}$ dependences on temperature at different oxygen partial pressure values are shown in the Fig. 2 and dilatometric curves for $Bi_4V_{1.5}Nb_{0.5}O_{11}$ — in the Fig. 3. An ideal structure can be described as built from alternating layers of $[Bi_2O_2]^{2+}$ and $[VO_{3.5-\delta}\square_{0.5-\delta}]^{2-}$. A decrease of the a cell parameter with PO_2 decreasing can be caused by oxygen vacancies concentration increase in 'equatorial' oxygen sites of the vanadium-oxygen layer [5,7,8].

It is well known that some BIMEVOX solid solutions with tetragonal γ-modification structure are characterized by structure transitions described as "order-disorder" transition from γ´- into γ-modification [7]. High-temperature in situ XRD investigation of different BIFEVOX samples did not reveal such type of transitions (Fig. 4) whereas dilatometric curves and temperature dependencies of conductivity contain inflection at about 700 K which can correspond to γ´-γ-transition. Slight linear dimensions change and a maximum point at thermal expansion factor curve are well seen on heating and cooling branches at 870–900 K. Combination of noted facts in a whole let make an assumption that some tetragonal BIMEVOX solid solutions with $x \geq 0.2$ at room temperature exist as ordered γ'-modification.

Electrical conductivity of BIMEVOX was investigated by means of impedance spectroscopy method. Typical complex impedance plots at different temperatures by the example of BINBVOX ($x = 0.15$) are shown in the Fig. 5. As it is well seen the shape of impedance diagram changes with temperature. At relatively low temperatures the complex impedance plot represents a semi-circle which transforms into a line that represents a beginning of another large semi-circle. The equivalent circuit for low-temperature region represents three parts in series: R1 resistance, and two Voight elements (R and CPE in parallel). R1 stands for volume resistance of the sample, R2 — for grain boundary resistance, CPE1 is a constant phase element that corresponds to charge transfer
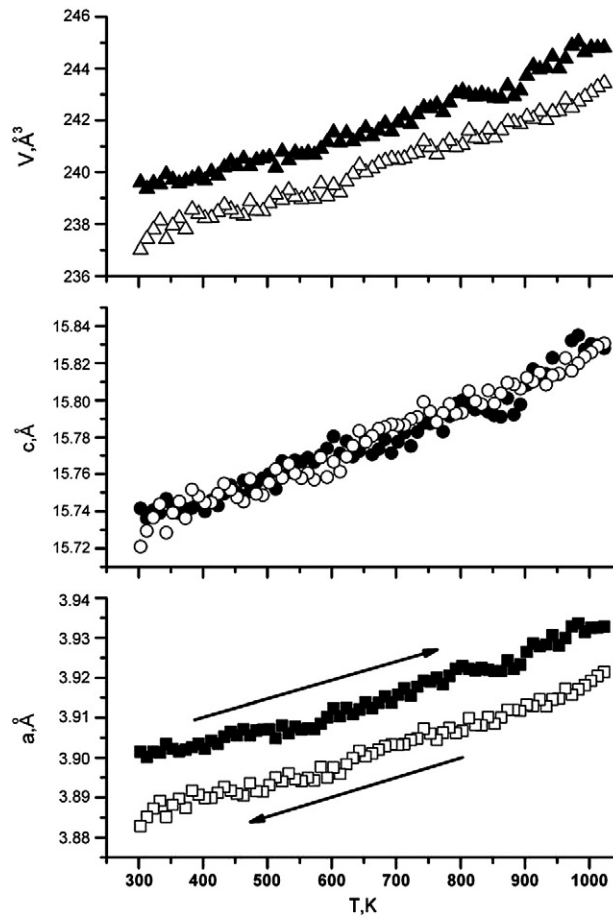
Fig. 2. Cell parameters of $Bi_4V_{1.4}Nb_{0.6}O_{11}$ depending on temperature. Black points - heating at $lgPo2=-0.67$, open points — cooling at $lgPo2= -2$ (bar).
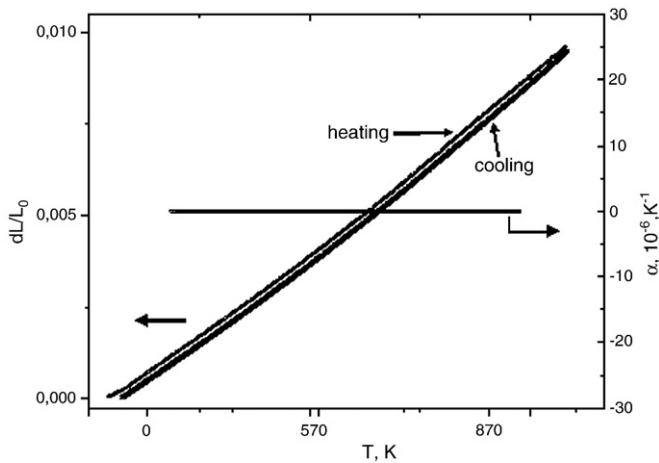

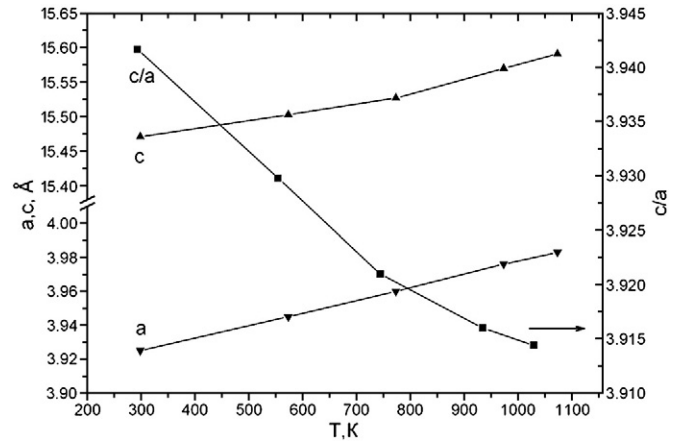**Fig. 3.** Dilatometric investigation data for $Bi_4V_{1.5}Nb_{0.5}O_{11}$.

Fig. 4. Temperature dependence of BIFEVOX cell parameters ($x=0.3$).

through grain boundaries, R3 and CPE2 describe complex processes which take place on the electrode-electrolyte border and inside the electrode. Capacities values for elements describing corresponding semi-circles are typical for volume conductivity component (10^{-11}–10^{-12} F) and grain boundary component (10^{-9}–10^{-10} F). R1 resistance stands for intragranular (volume) conductivity, parallel connection of R2 and CPE1 – for transfer through grain boundaries and Warburg element Ws and CPE2 – for electrode processes. Thus general conductivity is a sum of intragranular and grain boundaries conductivity. This value was used to determine conductivity of a polycrystalline sample.

Fig. 5a shows results of equivalent circuit modeling for BINBVOX ($x=0.15$) impedance spectra at 623 K.

Upon temperature increase the semi-circle which stands for grain boundary transfer disappears and complex impedance plot looks like semi-circle which transforms into a line that most likely is a characteristic of electrode processes. Equivalent circuit that stands for this type of complex impedance plots for $Bi_4V_{1.85}Nb_{0.15}O_{10.7-\delta}$ at 973 K is shown in Fig. 5b. In this case general conductivity is defined by R1 resistance only (comprising both bulk and grain boundary resistances).
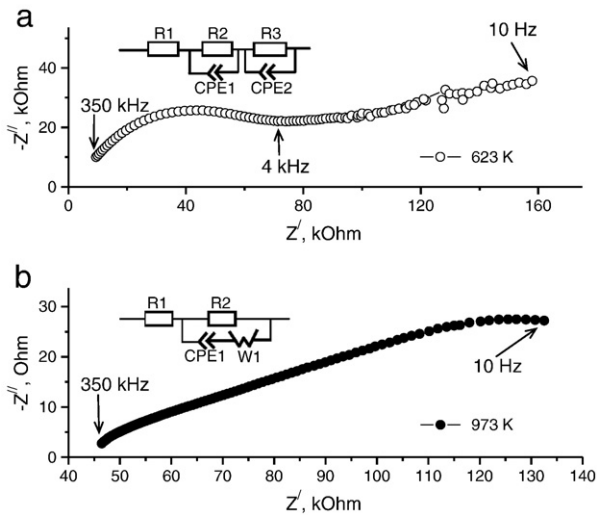
Fig. 5. Complex impedance plots and corresponding equivalent circuits change for $Bi_4V_{1.85}Nb_{0.15}O_{11}$ (PSC pyrolysis synthesis) depending on temperature: a) 623 K, and b) 973 K.

Examples of conductivity dependencies on temperature plotted on the basis of impedance measurements data are shown in the Fig. 6. The general shape of temperature conductivity curves of solid
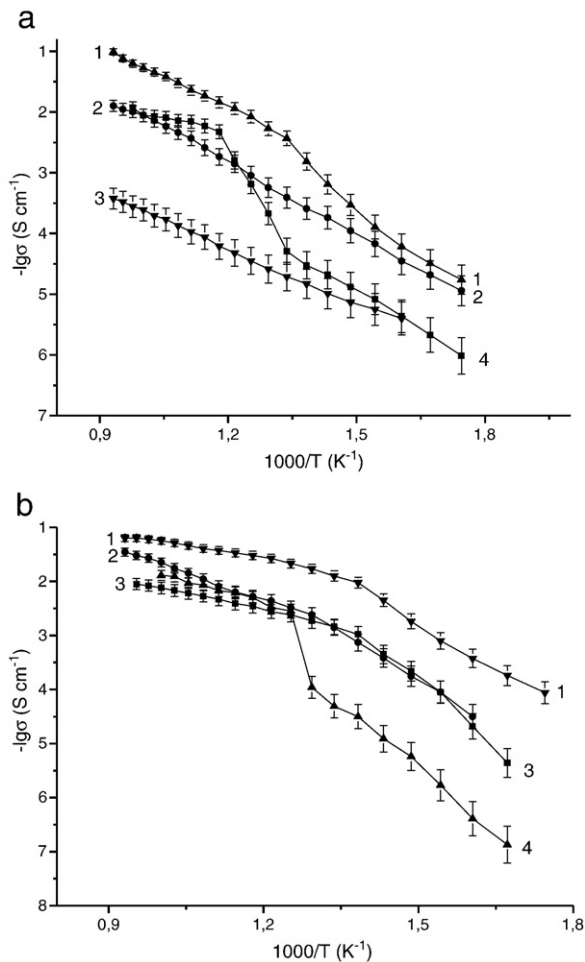
Fig. 6. Temperature dependency of total conductivity of BIMEVOX with different dopant concentration: a) 1 - $Bi_4V_{1.5}Fe_{0.25}Cr_{0.25}O_{10.5}$, 2 - $Bi_4V_{1.5}Fe_{0.5}O_{10.5}$, 3 - $Bi_4V_{1.5}Nb_{0.5}O_{11}$, 4 - $Bi_4V_2O_{11}$. b) 1 - $Bi_4V_{1.5}Fe_{0.1}Cr_{0.1}O_{10.8}$, 2 - $Bi_4V_{1.8}Fe_{0.2}O_{10.8}$, 3 - $Bi_4V_{1.8}Nb_{0.2}O_{11}$, 4 - $Bi_4V_{1.8}Cr_{0.2}O_{10.8}$.
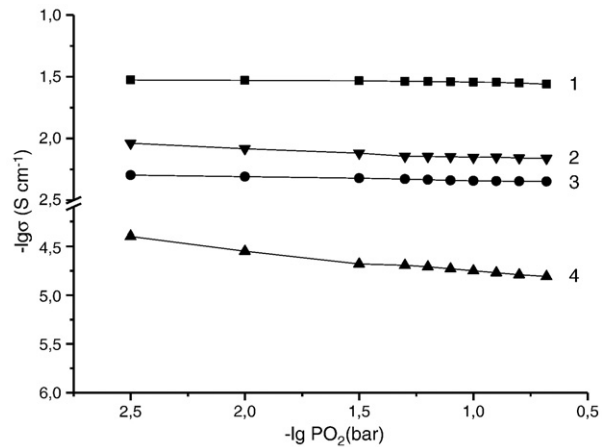
Fig. 7. $P(O_2)$-dependency of total conductivity BIMEVOX: 1 - $Bi_4V_{1.7}Fe_{0.3}O_{10.7}$, 973 K; 2 - $Bi_4V_{1.7}Fe_{0.3}O_{10.7}$, 873 K; 3 - $Bi_4V_{1.6}Nb_{0.4}O_{11}$, 1073 K; 4 - $Bi_4V_{1.7}Fe_{0.3}O_{10.7}$, 773 K.

solutions investigated is typical for BIMEVOX family. There are inflexions of lg σ–10^3/T curves from linear high-temperature to linear low-temperature region which are typical for solid solutions with low dopant concentration and they correspond to $\gamma \leftrightarrow \beta \leftrightarrow \alpha$ phase transitions for BIMEVOX. For the samples existing in γ-modification within the whole temperature region the curve is linear during heating as well as cooling with a slight change of conductivity activation energy at $\gamma \leftrightarrow \gamma'$ transitions.

Activation energy values of γ-modification solid solutions at high temperatures are equal to values of 0.2-0.4 eV which are typical for BIMEVOX family compounds. Transition to the ordered γ'-modification with temperature decrease is accomplished by increase of activation energy to 0.5–0.6 eV that coincides well with other results [9].

Change of oxygen partial pressure does not affect critically the shape of impedance spectra since complex impedance plots are described by the same equivalent circuits. For all solid solutions studied total conductivity measured does not depend on oxygen partial pressure in temperature range of 873–1023 K. For example, total conductivity of $Bi_4V_{1.7}Fe_{0.3}O_{10.7}$ and $Bi_4V_{1.6}Nb_{0.4}O_{11}$ plotted vs. oxygen partial pressure are shown in Fig. 7. Total conductivity was measured within rather narrow pO2 region and its slight dependence can be seen only for $Bi_4V_{1.7}Fe_{0.3}O_{10.7}$ at 773 K. This seems to be an evidence of that dominate charge carriers are oxide ions in spite of substitution of V by 3d metals which in principle could result in p-type conductivity increase. Aforementioned feature is common for BIMEVOX family solid solutions. For example, the oxide ions transfer number for BICUVOX doped with rare earth elements (La, Pr) was estimated by using EMF method in temperature range 370-1070 К [10]. The values of oxygen ions transfer number were found to vary between 0.9 and 0.99 at 780-910 К and they decrease with temperature increase. This behavior can be regarded as an evidence of dominant oxide ion transport in BIMEVOX solid solutions [5,10,11].

4. Conclusions

The solid solutions of BIMEVOX family (ME = Fe, Cr, Nb) were prepared as single phases. Compositions $Bi_4V_{2-x}Fe_xO_{11-\delta}$ (x = 0.2–0.5), $Bi_4V_{2-x}Nb_xO_{11-\delta}$ (x = 0.2-0.6) were found to keep a tetragonal γ-structure during temperature and oxygen partial pressure variations. Impedance spectroscopy study of the solutions prepared revealed that the solid solutions $Bi_4V_{2-x}Fe_xO_{11-\delta}$ (x = 0.3–0.5) have highest values of electrical conductivity as compared to other compositions investigated in wide range of temperature. The phases $Bi_4V_{2-x}Fe_{x/2}Cr_{x/2}O_{11-\delta}$ were shown to have enough high value of electrical conductivity but to exhibit temperature hysteresis of the unit cell parameters.

Acknowledgements

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