SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Some Features of the Preparation, Structure, and Properties of BICUTIVOX

E. S. Buyanova[a], M. V. Morozova[a], Yu. V. Emel'yanova[a], Z. A. Mikhailovskaya[a],
S. A. Petrova[b], R. G. Zakharov[b], N. V. Tarakina[c], and V. M. Zhukovskii[a]

[a] *Ural State University, pr. Lenina 51, Yekaterinburg, 620083 Russia*
[b] *Institute of Metal Physics, Ural Branch, Russian Academy of Sciences,*
ul. Sof'i Kovalevskoi 18, Yekaterinburg, 620219 Russia
[c] *Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences,*
ul. Pervomaiskaya 91, Yekaterinburg, 620219 Russia

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Abstract—This work continues the search for optimal preparation methods and studies of structural and transport characteristics of BICUTIVOX solid solutions of the general composition $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ ($x = 0.0-0.35$).

BIMEVOX materials are characterized by high oxygen ion conductivity at moderate temperatures. In the members of this family, the best conductivity values are most frequently encountered in high-temperature tetragonal γ phases. The high-temperature phase can be stabilized at room temperature by concurrent doping with cations of different valences [1−4]. Paydar et al. [1], for example, demonstrated the possibility of simultaneously doping copper and titanium cations to attain rather high electrical conductivity values. Alga et al. [2] described the niobium + copper binary substitution for vanadium with an overall doping level of 10%. Alga et al. thought that the solid solution of composition $Bi_4V_{1.8}Cu_{0.2-x}Nb_xO_{10.7-3x/2}$ with $0 < x < 0.05$ crystallizes in a tetragonal γ phase; with $0.1 < x < 0.15$, it forms a β phase. As x increases, unit cell parameters increase, too, and this is explained as arising from an increase in oxygen vacancy density in response to increasing niobium concentration. The electrical conductivity of $Bi_4V_{1.8}Cu_{0.15}Nb_{0.05}O_{10.625}$ exceeds the electrical conductivity of $Bi_4V_{1.8}Cu_{0.2}O_{10.7}$, which is doped with copper solely. Krok et al. [3] in their study of doubly substituted bismuth vanadate of composition $Bi_2V_{0.9}Co_yCu_{0.1-y}O_{5.35}$ with $0 < y < 0.1$ found that, in the low-temperature range, the conductivity systematically increases with increasing cobalt concentration. Paydar et al. [4] synthesized a $Bi_2V_{0.9}Cu_{0.1-x}Ti_xO_{5.35+x}$ ($0 \le x \le 0.1$) solid solution series. The compositions where $x = 0$, 0.025, or 0.05 were identified with the high-temperature γ phase of bismuth vanadate. The highest conductivity at 873 and 773 K was found in the composition with $x = 0.05$. At 573 K, however, the titanium-free composition $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ showed the highest conductivity. The authors believe that this result is due to the electronic

term of conductivity, and this term is higher for doubly (copper + titanium) doped solutions than for singly (copper) doped solutions.

BICUTIVOX solid solution is formed by the simultaneous substitution of copper and titanium for vanadium in the vanadium sublattice [5, 6]. The existence boundaries of polymorphs have been determined. Doping levels in the range $x = 0.025-0.15$ bring about crystal-lattice distortion, which is typical of $\alpha\text{-}Bi_4V_2O_{11}$ (space group $C2/m$), and symmetry lowering to triclinic. Only solid solutions of composition $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ ($0.25 \le x \le 0.30$) crystallize in a tetragonal unit cell of space group $I4/mmm$. Of the compounds studied, solid solutions with $x = 0.05$ have the highest conductivity above 873 K, which matches Paydar et al.'s data [4]. At lower temperatures, higher conductivity is observed for solid solutions where the γ phase is preserved in the low-temperature range. Solid-phase synthesis is mostly frequently used to prepare the above-described compounds; however, it fails to yield materials with sufficiently small particle sizes. Alternative synthetic methods include variants of preparing powders with the use of liquid precursors or mechanical activation of reagent mixtures [7, 8].

The main goal of this study is to prepare BICUTIVOX samples by various methods, to characterize them comprehensively, and to study their thermal stability in long-term heating/cooling cycles.

EXPERIMENTAL

To synthesize $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ ($x = 0.0-0.35$) solid solutions, we employed, apart from ordinary ceramic technology in the range 773−1073 K, mechanical activation and synthesis via liquid precur-

Table 1. Composition of power mixtures in mechanochemical treatment

τ, min	Composition
0.5	α-Bi_2O_3; V_2O_5; CuO; TiO_2
2	α-Bi_2O_3; Cu_3TiO_4; $Cu_3V_5O_4$; $Cu_2V_4O_{11}$; $TiVO_4$; $Bi_{20}TiO_{32}$; Bi_2CuO_4; $Bi_{7.38}Cu_{0.62}O_{11.69}$
4	$Bi_{3.8}V_{1.5}Ti_{0.7}O_{10.85}$; $Bi_{13}V_5TiO_{34}$; α-Bi_2O_3; $Cu_3V_2O_8$; Bi_2CuO_4; $Cu_{0.025}V_{0.975}O_2$; $Cu_{0.33}V_2O_5$
6	$Bi_{3.8}V_{1.5}Ti_{0.7}O_{10.85}$; $Bi_{1.9}(Cu_4V_4O_{16})$; $Cu_{1.9}V_{12}O_{29}$; Bi_2CuO_4; $Ti_7V_2O_{17}$; $Cu_{0.33}V_2O_5$
8	$Bi_{3.8}V_{1.5}Ti_{0.7}O_{10.85}$; $Bi_{1.9}(Cu_4V_4O_{16})$; $Cu_5V_2O_{10}$; $Cu_{0.33}V_2O_5$
13	$Bi_{3.8}V_{1.5}Ti_{0.7}O_{10.85}$; $Bi_{1.9}(Cu_4V_4O_{16})$; $Cu_{0.33}V_2O_5$
23	$Bi_{3.8}V_{1.5}Ti_{0.7}O_{10.85}$; $Bi_{4.1}Cu_{0.2}V_{1.7}O_{10.6}$; $Cu_{0.33}V_2O_5$
Annealing at 873 K	γ-$Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{10.7}$

sors. Oxides were mechanically treated in an AGO-2 planetary mill with the centrifugal factor $g = 60$ and a maximal action time of 23 min. For synthesis via liquid precursors, bismuth and copper nitrate solutions of required concentrations were prepared. Vanadium oxide was dissolved either in citric acid (in the ratio 1 : 3) to obtain vanadyl citrate $2(VO)C_6H_6O_7$ or in hydrogen peroxide. Titan was introduced in the form of tetrabutoxy- or tetraethoxytitanium ($C_{16}H_{36}O_4Ti$ or $C_8H_{20}O_4Ti$). Solutions were combined, then heated and concentrated to obtain a powdery intermediate. Final heat treatment was carried out at 873 and 1073 K. The phase composition of products was monitored by X-ray diffraction (DRON-3 diffractometer, CuK_α radiation, pyrolytic graphite on the reflected beam). Precision X-ray diffraction studies were carried out on a D8 ADVANCE diffractometer (βCuK_α radiation and a VÅNTEC area detector). Unit cell parameters were calculated and crystal structure were refined using TOPAS [9] and LMGP [10] program packages. Particle sizes were determined on a SALD-7101 Shimadzu particle size analyzer. Microstructures were examined using a JEOL JSM 6390LA scanning electron microscope equipped with a JED 2300 X-ray energy-dispersive microanalyzer. Elemental analysis was determined by inductively coupled plasma atomic emission on an iCAP 6500 Thermo Scientific spectrometer. Electrical conductivity was studied by impedance spectroscopy (Elins Z-2000 and Elins Z-350M impedance meters) from 1073 to 473 K.

RESULTS AND DISCUSSION

In our earlier work [6], $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ was synthesized using ceramic technology, where quenching from high to room temperatures at a cooling rate of ~250 K/min was employed to stabilize the high-temperature solid-solution phase. The high-temperature γ-BICUTIVOX phase (space group $I4/mmm$) at room temperature has been prepared only for compositions with $0.25 \leq x \leq 0.30$.

For the BIFEVOX family, we showed earlier [7] that synthesis via liquid precursors makes it possible to extend the range of existence of the γ phase and to attain smaller particle sizes and higher conductivities. Zyryanov [8] mentioned that mechanical activation is helpful in this context.

In order to determine the mechanochemical synthesis mechanism for $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ ($x = 0.1$, 0.3, 0.35) solid solutions, we analyzed diffraction patterns from mixtures that had been mechanically treated for different periods of time and after the final anneal at 873 K. Phase formation during mechanical activation (Table 1), as during solid-phase synthesis, passes through several consecutive stages. At the initial synthesis stage (within 6 min of activation), the starting oxide α-Bi_2O_3 remains in the batch; its content progressively decreases. Intermediates formed during the mechanochemical synthesis of BICUTIVOX are as follows: numerous and diverse copper vanadates, namely, $Cu_2V_4O_{11}$, $Cu_3V_5O_4$, $Cu_{0.33}V_2O_5$, and $Cu_{1.9}V_{12}O_{29}$; titanium vanadate $Ti_7V_2O_{17}$; double oxides, namely bismuth titanium oxide $Bi_{20}TiO_{32}$ and bismuth copper oxide Bi_2CuO_4; bismuth vanadium titanium oxide $Bi_{13}V_5TiO_{34}$; and bismuth, vanadium, and copper oxide $Bi_{1.9}(Cu_4V_4O_{16})$. This rich set of intermediate phases slightly differs from the set of intermediate phases in the solid-phase synthesis of BICUTIVOX or BIMEVOX with one dopant (copper or titanium). At middle synthesis stages of routine ceramic technology, double oxides of bismuth or vanadium are preferably formed with each of the substituent components (copper and titanium) [5]. In mechanochemical synthesis, contrary, triple oxides are formed with one of the substituent components, namely, $Bi_{3.8}V_{1.5}Ti_{0.7}O_{10.85}$ and $Bi_{4.1}Cu_{0.2}V_{1.7}O_{10.6}$, which then form BICUTIVOX upon heat treatment. The final product for the $x = 0.3$ composition after mechanical treatment and 3-h annealing at 873 K is the γ solid-solution phase. The $x = 0.1$ composition is formed in the low-temperature α phase.

Synthesis via liquid precursors followed by annealing 973 K yielded samples of composition

Table 2. Elemental composition of BICUTIVOX samples

x	Synthesis	Metal component ratio Bi : V : Cu : Ti		
		as-batch	SEM	AES
0.25	Solid phase	4.00 : 1.75 : 0.125 : 0.125	4.00 : 1.80 : 0.104 : 0.030	4.00 : 1.70 : 0.127 : 0.034
	Via Precursors		4.00 : 1.57 : 0.120 : 0.112	4.00 : 1.58 : 0.119 : 0.090
0.3	Mechanochemical	4.00 : 1.70 : 0.150 : 0.150	4.00 : 1.68 : 0.255 : 0.148	4.00 : 1.64 : 0.150 : 0.095

$Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-x}$ ($x = 0.25, 0.3$), which were iso-structural to γ-$Bi_4V_2O_{11}$. As for the BIFEVOX family [7], BICUTIVOX formation in synthesis via liquid precursors occurs in a similar way as phase formation in solid-phase synthesis. In a primary precipitate, there is bismuth vanadate of composition $BiVO_4$. Upon subsequent calcination at 773 K, the reaction mixture acquires a more complex composition because of the appearance of copper vanadates and bismuth titanates. The interaction of components to form a single-phase product within the homogeneity region ends at temperatures 100–150 K lower than during solid-phase synthesis. Compositions where $x < 0.25$ do not crystallize in the tetragonal unit cell of γ-$Bi_4V_2O_{11}$. When $x \geq 0.35$, samples contain the γ solid-solution phase and minor $BiVO_4$.

Thus, unlike for BIFEVOX [7], neither mechanical activation, nor solution synthesis extends the existence region of the high-temperature γ-BICUTIVOX phase, nor it extents the homogeneity range as a whole. However, for the γ phase to be stabilized in the same range of compositions ($0.25 \leq x \leq 0.30$) at room temperature in synthesis via liquid precursors and mechanical activation, quenching is not required.

The particle size of powders varies in the range 0.5–15 μm regardless of composition. This means that synthesis via liquid precursors can yield powders with smaller grain sizes than solid-phase synthesis (3–30 μm). Mechanochemical synthesis yields powders with a wider grain size range(0.5–30 μm), but with a greater small particle fraction with sizes of 1–5 μm.

To characterize samples prepared by different methods, we studied near-surface microstructure and in the bulk of sintered briquettes using scanning electron microscopy (SEM). Regardless of the synthesis method, we discovered that titanium atoms nonuniformly enter the crystal lattice of the solid solution to form uncontrolled titanium-rich microimpurity phases that are detectable only by electron probe microanalysis. This interferes with the results of elemental analysis, which gives an underestimated overall titanium content in the solid solutions compared to the calculated values. Table 2 displays formula indices determined by various methods for some samples prepared by different methods.

Figure 1 shows a SEM image of a polished section of a $Bi_4V_{1.75}Cu_{0.125}Ti_{0.125}O_{11-\delta}$ tablet (prepared by solution synthesis), which illustrates the occurrence of titanium-rich near-surface grains in the briquette.

Similar inclusions are also detected in cleaved surfaces of briquettes, proving that microimpurities are distributed over the entire bulk of the briquette. On the other hand, an impurity phase is not detected in a cleaved surface or a polished section of a $Bi_4V_{1.75}Cu_{0.125}Ti_{0.125}O_{11-\delta}$ briquette prepared by solid-phase synthesis. A second, minor phase is detected by X-ray diffraction only in the $x = 0.30$ composition in an amount of ~1%, and this amount increases as x increases further [6]. This phase, as the major phase, too, may be described in terms of a tetragonal unit cell (*I4/mmm*) with unit cell parameters close to the parameters of the major phase; most likely, this is a solid solution which also belongs to the BIMEVOX family but with one dopant. This inference in general agrees with the SEM and AES results presented in this work. Even within the BICU-TIVOX homogeneity region which was determined by precision X-ray diffraction studies, titanium (unlike copper) only partially occupies vanadium positions. The remnant atoms can form a minor phase the composition of which is most likely to vary, in ratios between titanium, copper, and vanadium atoms, from titanium oxide with a small vanadium amount to a titanium-substituted BIMEVOX solid solution.
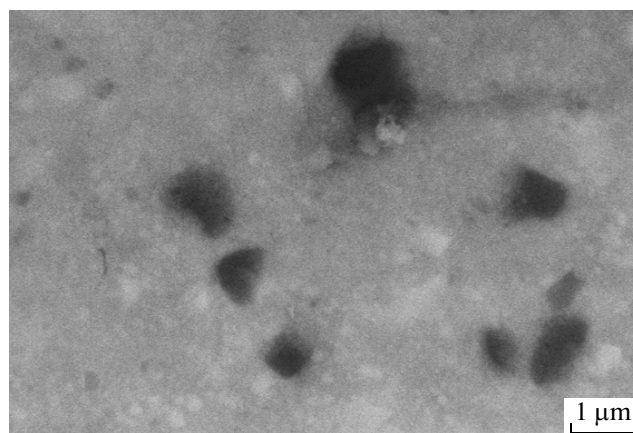

1 μm

Fig. 1. Scattered electron image of a section of a $Bi_4V_{1.75}Cu_{0.125}Ti_{0.125}O_{11-\delta}$ briquette. Contrast is due to the differentiated chemical composition: darker regions, which correspond to titanium oxide, are distributed over a complex bismuth vanadate matrix. The average inclusion size: ~1 μm.

Table 3. Structural parameters for mechanochemically prepared $Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{10.7}$, space group $I4/mmm$, $a = 3.9313(5)$ Å, $c = 15.4472(3)$ Å, $V = 238.748(7)$ Å^3

Atom	Multiplicity	x	y	z	Occupancy	B_{iso}, Å^2
Bi	4	0.0	0.0	0.1684	1.13	1.38
V/Ti	4	0.5	0.5	0.0012	0.46	0.93
Cu	4	0.5	0.5	0.0012	0.03	0.93
O(1)	4	0.0	0.5	0.25	0.91	1.02
O(2)	4	0.5	0.5	0.0985	0.55	1.02
O(3)	8	0.5	0.0	0.0365	0.38	1.02
O(4)	16	0.5	0.3365	−0.0134	0.27	1.02
GOOF = 2.30; $R_{wp} = 6.65\%$, $R_p = 5.54\%$, $R_{Bragg} = 2.466\%$						

As the initial model for structure refinement in mechanochemically prepared $Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{10.7}$, we used a solid solution of composition $Bi_2V_{0.9}Co_{0.1}O_{5.35}$ (space group $I4/mmm$, $a = 3.9225(2)$ Å, $b = 15.4470(8)$ Å) [11]. Inasmuch as titanium and vanadium are undistinguishable by X-rays due to the closeness of their atomic form-factors, they were considered as one metal in the calculations. The initial occupancy was derived from the chemical composition. Reflection broadening analysis showed anisotropic dimensional broadening. The results of unit cell parameter calculations are displayed in Table 3. The excess of oxygen is due to the mechanochemical synthesis, where the sample can additionally oxidize in air because of having a developed surface (a coherent scattering block was estimated at less than 200 nm). The same factor can be responsible for a small overpopulation of the bismuth position on the assumption of the occurrence of bismuth(V) atoms. The titanium

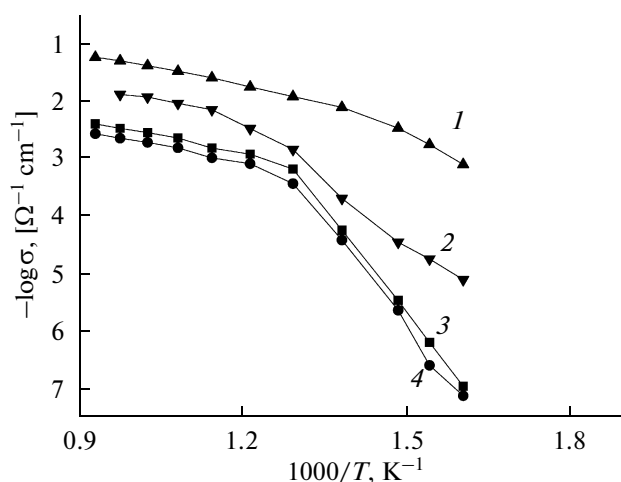**Fig. 2.** Electrical conductivity versus temperature for $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ samples synthesized by various methods: (*1*) solid-phase synthesis, $x = 0.3$; (*2*) mechanically activated synthesis, $x = 0.3$; (*3*) solid-phase synthesis, $x = 0.25$; and (*4*) solution synthesis, $x = 0.25$.

content of the sample is also lower than the calculated value (Table 2).

To ascertain the thermal stability of BICUTIVOX polymorphs in heating/cooling cycling, we carried out long-term stepped anneals of samples that initially were in the α- or γ phase at room temperature. Samples were consecutively annealed at 723, 823, 923, 973, 1023, and 1083 K for two weeks at each step and in the reversed mode where slowly cooling samples were monitored by X-ray diffraction. Annealing temperatures were selected with account for possible phase transitions in BICUTIVOX, which were determined earlier by X-ray diffraction and dilatometric studies: 730−750 K for the α → β transition and 770−820 K for the β → γ transition [6].

After annealing at 823 K, X-ray diffraction patterns of α-$Bi_4V_{1.95}Cu_{0.025}Ti_{0.025}O_{10.95}$ and γ-$Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{10.7}$ featured, in addition to the reflections from the major BICUTIVOX solid solution, reflections from impurities: $BiVO_4$ in an amount of ~4% and $Bi_{3.5}V_{1.2}O_{8.25}$ in an amount of ~1% for $x = 0.05$ and 6% for $x = 0.30$. The mixture completely transforms into BICUTIVOX at 923 K in both compositions. Upon a further rise in temperature and annealing at 1083 K, α-$Bi_4V_{1.95}Cu_{0.025}Ti_{0.025}O_{10.95}$ experiences a phase transition $P\bar{1} \rightarrow I4/mmm$; that is, transforms into the γ phase. In reversals, that is, upon consecutive temperature reduction, at 1023 K the high-temperature γ phase again transforms into the low-symmetry triclinic phase, and the cell symmetry does not change further. The results obtained for $Bi_4V_{1.95}Cu_{0.025}Ti_{0.025}O_{10.95}$ fairly correlate with in situ high-temperature X-ray diffraction data for α-BICUTIVOX [6].

For γ-$Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{10.7}$, two consecutive phase transitions were detected upon anneals with temperature rising: $I4/mmm$ (723 K) $\rightarrow P\bar{1}$ (823 K) $\rightarrow I4/mmm$ (923 K). A further rise in temperature did not bring about any change in symmetry group. Noteworthy, as shown by high-temperature powder X-ray diffraction [6], the structure type of γ-$Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{10.7}$ does not change upon heating at 0.5 K/s.
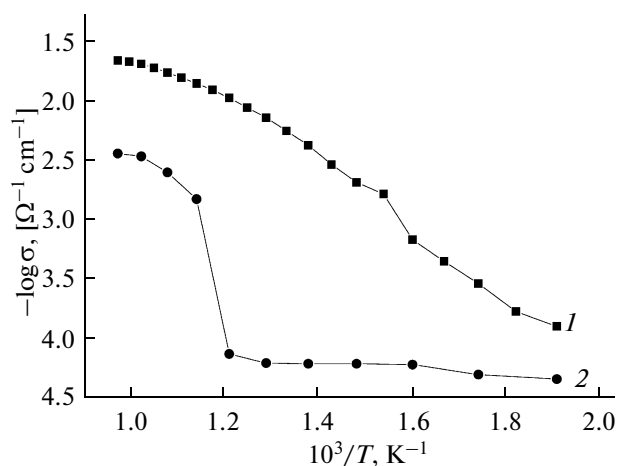
Fig. 3. Electrical conductivity for $Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{11-\delta}$ samples: (*1*) a single-phase sample and (*2*) a sample containing a TiO_2 impurity.

Thus, regardless of whether the γ-phase of solid solutions is in any way stabilized at room temperature in the BICUTIVOX system, anneals show that its further continued existence in a steady state is impossible.

The electrical conductivity in BICUTIVOX was studied by impedance spectroscopy using platinum electrodes. Impedance spectra for BICUTIVOX cells are typical of oxygen ion conductors [6]. An equivalent cell scheme corresponding to the processes occurring within a certain temperature range was selected using Zview software (Version 2.6b, Scribner Associates, Inc.). Figure 2 shows conductivity curves derived from impedance measurements for $Bi_4V_{2-x}Cu_{x/2}Ti_{x/2}O_{11-\delta}$ samples prepared by various technologies. The highest electrical conductivity is observed in the $x = 0.3$ composition synthesized by solid-phase technology, which agrees with our earlier data [6]. Further, for this sample a small inflection on the $\log\sigma - 1000/T$ curve was noticed at ~710 K, which corresponds to transition to the ordered γ' phase upon cooling and appears at rather high recording rates (this is also in agreement with [6]). For other samples, the $\log\sigma - 1000/T$ curves each feature a break at 770 K characterizing a first-order polymorphic transition to the low-temperature phase. Samples synthesized by solution technology, unlike the BIFEVOX system [7], are not substantially

better in conductivity values; this is likely due to the impossibility of stabilizing the γ-BICUTIVOX phase over a wide temperature range.

Microimpurities deteriorate both the mechanical properties of a sample via increasing its brittleness and the conductivity by decreasing the integrated bulk conductivity of BIMEVOX (Fig. 3).

To summarize, despite nice values of the overall electrical conductivity in some representatives of the BICUTIVOX family, there are some challenges in manufacturing and using these materials. These challenges arise from the appearance of uncontrolled impurities during the synthesis and the impossibility of attaining a tailored composition of the resulting samples and stabilizing the high-conductivity γ-BICUTIVOX phase over a wide temperature range and with varying thermodynamic parameters of the medium.

ACKNOWLEDGMENTS

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