



Structural and transport properties of doped bismuth titanates and niobates

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ARTICLE INFO

Keywords:

Bismuth titanates/niobates

Structure

Conductivity

Oxygen mobility

ABSTRACT

Cobalt- or Zn-doped bismuth titanates and Mg + Cu-doped bismuth niobate were synthesized by the method of organic-inorganic precursors combustion. Distribution of dopants over the sites of the pyrochlore structure was elucidated by X-ray powder diffraction structure refinement and pycnometric density analysis. Zinc and cobalt cations are mainly located in Bi sites appearing also in Ti sites at their high content. Mg cations are located only in Nb sites, while Cu cations are equally distributed between Bi and Nb sites. Magnetic susceptibility data confirm Co^{2+} state of cobalt atoms revealed by NEXAFS. Antiferromagnetic exchange appears when Co atoms enter the titanium sites. Electronic conductivity of *p*-type dominates for Co-doped samples in the 160–750 °C temperature range. The oxygen mobility and surface reactivity were studied by the oxygen isotope hetero-exchange with C^{18}O_2 in isothermal and temperature-programmed modes. Mobility of the lattice oxygen can be described by a homogeneous model. The oxygen mobility and surface reactivity are comparable for doped bismuth titanates and niobates correlating with conductivity and being the highest for Co and Cu-doped samples with disordered distribution of dopants between lattice sites.

Classification codes: A6630L

A7280G

A8120E

A8170J

B2130

B2520E

1. Introduction

In the last decades compounds with the pyrochlore structure based on bismuth oxide –mixed titanates or niobates [1,2] attracted increased attention due to new possibilities of their application. Thus, zinc-containing bismuth niobates with a high dielectric constant $\epsilon \sim 154$ [3] are promising for producing multi-layer capacitors; manganese and cobalt-containing bismuth niobates were investigated with the purpose of detection of multiferroic ordering in them [4,5]. Doped bismuth titanates are interesting from the point of view of their luminescent [6,7], photocatalytic [8,9] and dielectric [1,10–11] properties.

Bismuth titanate, $\text{Bi}_2\text{Ti}_2\text{O}_7$, is interesting as a material for capacitors owing to its high dielectric constant, low dielectric losses and a low temperature coefficient of capacitance. However, its practical application is limited by the decomposition at $T > 650^\circ\text{C}$ [1,12] and co-

existence of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [13] and $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ [14] phases. In previous studies it was shown that doped bismuth titanate pyrochlores $\text{Bi}_{1.6}\text{M}_x\text{Ti}_2\text{O}_7 - \delta$ ($M = \text{Cr, Cu, Mn, Fe, Mg, Zn, Sc}$) are stable up to the melting temperature [15–18].

For $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ pyrochlore structure with the $Fd\bar{3}m$ space group, A-sublattice sites located in $16c \rightarrow 96h$, $96g$ Wyckoff positions can be occupied by Bi as well as dopant cations. B-sublattice sites located in $16d$ Wyckoff positions can be occupied by Ti or Nb as well as dopant cations. The oxygen sublattice is nonuniform and divided into O ($48f$ positions) and O' ($8a \rightarrow 32e$ positions) sublattices. The dopant atoms at $x < 0.3$ are predominantly located in the bismuth sites of the $\text{Bi}_{1.6}\text{M}_x\text{Ti}_2\text{O}_7 - \delta$ structure. At $x > 0.3$ they are partially distributed over the titanium sites [16–18]. In chromium-containing $\text{Bi}_{1.6}\text{Cr}_x\text{Ti}_2\text{O}_7 - \delta$ system the homogeneity region is narrow, x varies from 0.04 to 0.12 and chromium atoms in this system are located in the

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Bi sites. A mixed ionic-electronic conductivity was found in $\text{Bi}_{1.6}\text{M}_x\text{Ti}_2\text{O}_{7-\delta}$ ($M = \text{Cr, Fe, Cu, Mn}$) systems [15–18]. When 3d element dopants are distributed over B-sites, dominating electronic type of conductivity dominates and antiferromagnetic superexchange for dopants was observed [16]. So, the presence of substituting cation can be also crucial for the relaxation process in doped bismuth titanates and niobates [19]. In a recent study of oxygen diffusion by the oxygen isotope heteroexchange in bismuth titanium pyrochlores doped with magnesium, scandium and copper we have shown that already at 350 °C a fast oxygen transport occurs [20].

The aim of this work is elucidating effect of transition metal nature and cation distribution on composition, structure and transport characteristics of bismuth based pyrochlores. Doped Bi niobates/titanates solid solutions were prepared and their synthesis procedures were optimized to obtain fine powders and functional ceramics possessing required phase stability in certain conditions (temperature, pressure, content of dopants, etc.). Distribution of dopants between two types of cation positions in the pyrochlore structure was studied. The magnetic properties of materials obtained were investigated and factors affecting their magnetic behavior and clustering of paramagnetic atoms were elucidated. Conductivity of materials was estimated depending on the temperature, dopant content and the oxygen partial pressure. Oxygen transport properties were studied using oxygen isotope heteroexchange with C^{18}O_2 .

2. Materials and methods

Co- and Zn-doped bismuth titanates $\text{Bi}_{1.6}\text{Zn}_{0.2}\text{Ti}_2\text{O}_{7-\delta}$, $\text{Bi}_{1.6}\text{Co}_x\text{Ti}_2\text{O}_{7-\delta}$ ($0.08 \leq x \leq 0.40$) and mixed Mg-Cu-containing bismuth niobate $\text{Bi}_{1.6}\text{Mg}_{0.4}\text{Cu}_{0.4}\text{Nb}_{1.6}\text{O}_{7-\delta}$ were synthesized by the method of organic-inorganic precursors combustion. The pyrochlore structure $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ is formed when relation of ionic radii of all atoms in A sites to ionic radii of all atoms in B sites is in the range of 1.46–1.78 [1]. This factor is a main reason for synthesis of bismuth deficient titanates in our work. For the synthesis bismuth nitrate pentahydrate, $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%)], cobalt nitrate hexahydrate, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%)], magnesium nitrate hexahydrate, $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%)], zinc nitrate hexahydrate, $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%)], copper nitrate trihydrate, $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9%)], anatase $[\text{TiO}_2$ (99.99%)], niobium oxide $[\text{Nb}_2\text{O}_5$ (99.9%)] were used as starting materials and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) as reagent. According to SEM analysis, the size of TiO_2 and Nb_2O_5 agglomerates was in the range of 50–100 nm. At first we heated the stoichiometric mixture of nitrates crystallohydrates to melting, added TiO_2 or Nb_2O_5 powders and then mixed with citric acid in the necessary ratio. After heating and stirring a gel-like phase forms, which burns out to give a powder. According to X-ray analysis, 30–40% of the pyrochlore phase is present in thus obtained powders. Then powders were pelleted and calcined under air till the X-ray patterns remained unchanged. The last temperature of annealing of $\text{Bi}_{1.6}\text{Mg}_{0.4}\text{Cu}_{0.4}\text{Nb}_{1.6}\text{O}_{7-\delta}$ was 1050 °C (20 h).

The phase composition and structure of compounds were studied by X-ray method on a SHIMADZU XRD-6000 diffractometer using CuK_α radiation with $\lambda = 1.54056$ nm within the angle range 10–80° (the step 0.05°) at the exposure time 2 s. Distribution of dopants in the sites of the pyrochlore structure was determined by fitting their X-ray diffraction pattern with Rietveld analysis. Scanning electron microscopy (SEM) was carried out on a TESCAN VEGA 3 SBU microscope. The local composition and morphology of samples were studied for polished pellets by EDX analysis with a X-ACT (EDS) micro analyzer. DSC and TG analysis of powdered samples were carried out in air in platinum crucibles with heating (to 1300 °C) and subsequent cooling (to 600 °C) rates of 5 °C/min using NETZSCH STA 409 PC/PG. The NEXAFS (near edge X-ray absorption fine structure) spectra of the Co2p absorption edge of bismuth cobalt titanate pyrochlores and cobalt oxides (CoO , Co_2O_3) were obtained using synchrotron radiation on a BESSY-II (Berlin) device [21]. All of the spectra were recorded in the total

electron yield (TEY) mode. Magnetic susceptibility was measured by Faraday method in the temperature range of 77–400 K. The error of the method does not exceed 1%. The electric properties were studied for samples pressed into pellets. The electrodes were prepared from highly dispersed silver oxide applied onto both surfaces of the pellets and annealed at 700 °C during 30 min. Capacitance and dielectric loss tangent were measured in different gases: argon, $p(\text{O}_2) = 0.01$ atm; air, $p(\text{O}_2) = 0.21$ atm; oxygen, $p(\text{O}_2) = 0.99$ atm. The thermoelectric effect of samples (the Seebeck coefficient) was determined by a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across the material. The temperature difference between two silver electrodes was 30–40 °C. Temperature dependent dielectric measurements were made using a Z-1000P (Elins) impedance analyzer. An applied ac voltage was 10 mV. The measurements were made from room temperature to 600 °C in a frequency range of 1–10⁶ Hz. To determine the oxygen ion transference numbers electrochemical cell was used. Gas-tight ceramic discs with silver electrodes were sealed hermetically onto a dense tube. Oxygen (0.99 atm) was pumped into the internal volume of the tube, atmospheric pressure was on the other side. The measurements were performed at temperatures from 400 to 750 °C.

The oxygen mobility and surface reactivity of the ground samples were studied by using the temperature-programmed isotope exchange (TPIE) with C^{18}O_2 in closed and flow reactors. The pretreatment was carried out at 700 °C in 1% $\text{O}_2 + \text{He}$ during 30 min, while the exchange was made in 1% $\text{C}^{18}\text{O}_2 + \text{He}$ mixture at 50–800 °C with 5 °C/min ramp. The gas phase composition was analyzed by using SRS QMS200 mass spectrometer (Stanford Research Systems, USA) for the experiments in a closed reactor and UGA-200 mass spectrometer (Stanford Research Systems, USA) for the experiments in a flow reactor. Time dependencies of $\text{C}^{16}\text{O}^{18}\text{O}$ molecules fraction $f_{16-18}(t)$ and ^{18}O atoms fraction $\alpha(t)$ (referred to as isotope kinetic curves) were analyzed by using isotope kinetic equations [22–24].

The authors undersign, certificate that the procedures and the experiments they've done respect the ethical standards in the Helsinki Declaration of 1975, as revised in 2000 (5), as well as the national law.

3. Results and discussion

3.1. Structure and morphology features

Single phase $\text{Bi}_{1.6}\text{Zn}_{0.2}\text{Ti}_2\text{O}_{7-\delta}$, $\text{Bi}_{1.6}\text{Co}_{0.23}\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Bi}_{1.6}\text{Mg}_{0.4}\text{Cu}_{0.4}\text{Nb}_{1.6}\text{O}_{7-\delta}$ samples with the pyrochlore type structure were obtained (Fig. 1). All X-ray diffraction patterns exhibit only characteristic peaks of the pyrochlore phase [25]. The homogenous ranges of $\text{Bi}_{1.6}\text{Co}_x\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Bi}_{1.6}\text{Zn}_x\text{Ti}_2\text{O}_{7-\delta}$ are $0.08 \leq x(\text{Co}) \leq 0.23$ and $0.1 \leq x(\text{Zn}) \leq 0.5$, respectively [26]. As can also be seen in the SEM images of polished surface (Fig. 2) any admixtures in obtained ceramics are absent. The composition of samples derived from EDX data (in brackets of Fig. 2 caption) corresponds to the initial one.

On the base of DSC and TG data it was determined that the melting point correspond to 1235 °C for $\text{Bi}_{1.6}\text{Zn}_{0.2}\text{Ti}_2\text{O}_{7-\delta}$, 1226 °C for $\text{Bi}_{1.6}\text{Co}_{0.23}\text{Ti}_2\text{O}_{7-\delta}$, and 1096 °C for $\text{Bi}_{1.6}\text{Mg}_{0.4}\text{Cu}_{0.4}\text{Nb}_{1.6}\text{O}_{7-\delta}$ powders.

To refine the structure of compounds, analysis of the X-ray patterns by Rietveld method was carried out. For this analysis $\text{Bi}_{1.6}\text{Co}_{0.16}\text{Ti}_2\text{O}_{7-\delta}$, $\text{Bi}_{1.6}\text{Zn}_{0.2}\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Bi}_{1.6}\text{Mg}_{0.4}\text{Cu}_{0.4}\text{Nb}_{1.6}\text{O}_{7-\delta}$ X-ray diffraction patterns were chosen. We fixed the occupation of atom sites in correspondence with the quantitative composition of the sample, while temperature parameters were varying. According to Esquivel-Elizondo et al. [1], in $\text{Bi}_2\text{Ti}_2\text{O}_7$ bismuth atoms are shifted from 16c sites to 96h or 96g sites, that was applied in our refinement.

For $\text{Bi}_{1.6}\text{Co}_{0.16}\text{Ti}_2\text{O}_{6.56}$ the best agreement between theoretical and experimental X-ray patterns was obtained for cobalt atoms being distributed over bismuth sites (Table 1). In Fig. 3 the experimental and

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