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Synthesis, Structure, and Investigation of Bismuth Niobate Doped by Alkaline-Earth Elements

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Abstract

Polycrystalline samples with general formula $Bi_{3-x}M_xNbO_{7-\delta}$ (M = Ba, Ca, Mg, or Sr; x = 0, 0.1) were obtained by solid state method. Single phase compounds are niobates doped by strontium and calcium. A major phase has a tetragonal structure (space group I-$4m2$) after annealing at 850°C, which completely transfers into a cubic one (space group $Fm3m$) after 1000°C. Dense sintered ceramics were prepared with thermal expansive coefficient equal to 10×10^{-6} °C^{-1}. The electroconductivity values of the pure bismuth niobate with a tetragonal structure are higher than those of the one with a cubic structure. However, such tendency does not remain for the bismuth niobate doped by calcium.

Keywords: bismuth niobate, alkaline earth elements, structure, oxide ion conductivity

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1. Introduction

At the present time, scientists and engineers are actively searching for new materials, which can be perspective for their application in different electrochemical devices, such as fuel cells, gas sensors, and membranes. Among all the variety of complex oxide materials, a special place is kept by delta (δ) modification of bismuth oxide as it was shown in [1]. Due to a high content of oxygen vacancies (25%), the electroconductivity values of δ-Bi_2O_3 are two orders of magnitude higher than those obtained for yttrium stabilized zirconium dioxide, being equal to 1 Ohm^{-1}cm^{-1} [1]. But there is one main disadvantage – the temperature interval of existing δ-phase is limited by 730–825°C. So a high temperature phase needs to be stabilized at room temperature, for example, by doping bismuth oxide with different suitable cations like niobium, tantalum, tungsten, and other. As shown in [2], the number of oxygen vacancies in the cubic structure

decreases dramatically during bismuth niobate formation in comparison with δ-phase. Hence, the electroconductivity falls as well. On the other hand, a formation of rhombohedral structure was observed while doping bismuth oxide by alkaline earth ions (Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}) [1, 3]. This phase has oxide ion conductivity values comparable with δ-Bi_2O_3. As was reported, the values are higher at larger ionic radius of a replacement ion (r (Ca^{2+}) = 1.26 Å, r(Sr^{2+}) = 1.40 Å, r(Ba^{2+}) = 1.56 Å [4]). As for bismuth niobate doped by alkaline earth elements, big concentrations of such dopants lead to generation of compounds with pyrochlore structure. The compositions $CaBi_2Nb_2O_9$, $SrBi_2Nb_2O_9$, and $Bi_{1.5}MgNb_{1.5}O_7$ were described as dielectrics in [5–7]. There have been no data in the literature about the investigation of an influence of low level doping on structure and electroconductivity of bismuth niobate Bi_3NbO_7.

Therefore, the aim of the present work is preparation of bismuth niobate doped by alkaline earth elements, as well as research of synthesis conditions influence on its structure, determination of its phase composition, possibility of a solid solution formation, and electroconductivity measurements of the electrolyte materials.

2. Methods

The samples with general formula $Bi_{3-x}M_xNbO_{7-\delta}$ (M = Ba, Ca, Mg, or Sr; x = 0, 0.1) were obtained by solid state method. Bi_2O_3 (> 99.99%), Nb_2O_5 (> 99.99%), $CaCO_3$ (> 99.9%), $BaCO_3$ (> 99.9%), $MgCO_3$ (> 99%), and $SrCO_3$ (> 99.99%) were taken as initial compounds. Synthesis was performed at temperature range 600–1000°C with intermediate regrinding via 50–100°C. The holding time at each stage was 8 hours. The obtained powders were checked by X-ray diffraction analysis (XRD) (automatic diffractometer DRON-UM1, $Cu_{K\alpha}$-radiation, monochromator from pyrolitic graphite on reflected beam) after annealing at 850, 950, and 1000°C. XRD patterns of the samples were collected in the range 2θ = 5–72° with speed equal to 2 degrees per minute. A phase composition of all sintered specimens was calculated using database ICDD PDF 4 and full profile analysis with Rietveld method. For further investigations, powder samples were pressed and sintered into briquettes at 850 and 1000°C during 8 hours. A surface morphology and a local chemical composition of the ceramic specimen fired at 1000°C was determined using scanning electron microscopy (SEM) on microscope JEOL JSM 6390LA (Jeol, Japan), equipped with a prefix for local energy dispersive X-ray (EDX) microanalysis (energy dispersive microanalyzer JEOL JED 2300, Jeol, Japan). A value of thermal expansive coefficient (TEC) of the single phase sample was calculated using dilatometric analysis (dilatometer DIL 402 C, Netzsch, Germany) in the temperature

range 30–1000°C with heating speed equal to 2 degrees per minute. The electroconductivity measurements of the samples sintered at 850 and 1000°C were carried out by impedance spectroscopy method (impedance meter Z-3000 'Elins', Russia) using two-probe cell with platinum electrodes in the temperature range 850–200°C at cooling regime. Obtained impedance spectra were treated with 'ZView' software and equivalent schemes were fitted to them. Using these data, the temperature dependences of electroconductivity (σ) were plotted in Arrhenius coordinates -lgσ – 1000/T.

3. Results

According to the results of XRD analysis, it is obvious that the generation of single phase compounds is possible by doping bismuth niobate by alkaline earth elements with general formula $Bi_{3-x}M_xNbO_{7-\delta}$ (M = Ba, Ca, Mg, or Sr; x = 0, 0.1) only in the case of using calcium (at 850 and 1000°C) and strontium (only at 850°C). The synthesis temperature has significant influence on the structure of the samples. After annealing at 850°C, bismuth niobate has a tetragonal structure with space group (S.G.) *I-4m*2. As temperature increases, an additional cubic structure (S.G. *Fm*3*m*) appears, which completely replaces the first one at 1000°C (Figure 1). The similar behavior of pure bismuth niobate was described in [8]. The full phase composition of the sintered samples is specified in Table 1. Impurities were found after synthesis at 850°C $BaNb_2Bi_2O_9$ (4%) and $Mg_{0.7}Nb_{15.2}Bi_{16.67}O_7$ (2%). Decomposition of $Bi_{2.9}Sr_{0.1}NbO_{7-\delta}$ occurred at higher temperature with formation of $SrNb_2Bi_2O_9$ (8%). The unit cell parameters were calculated for all single phase compounds (Table 2).

Further, the obtained powders were pressed and sintered into briquettes. It was shown for the sample with composition $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ sintered at 1000°C that high density ceramics with small spherical pores was formed (Figure 2). The sample had a homogeneous element composition. According to EDX spectra, an insignificant bismuth sublimation takes place during high temperature synthesis. At the same time, there are no phase transitions on temperature dependence of linear sample sizes of the $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ with cubic structure. A small difference between heating and cooling curves deals with additional sintering of the sample at high temperatures. TEC of the $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ is equal to $10{\times}10^{-6}\,°C^{-1}$ (Figure 3). The electroconductivity values were determined for both series of the samples with tetragonal and cubic structures.

The impedance spectra obtained during measurements (Figure 4) can be described by different corresponding sequences of such elements as resistivity (R) and constant phase element (CPE), which are used for description of different complex processes
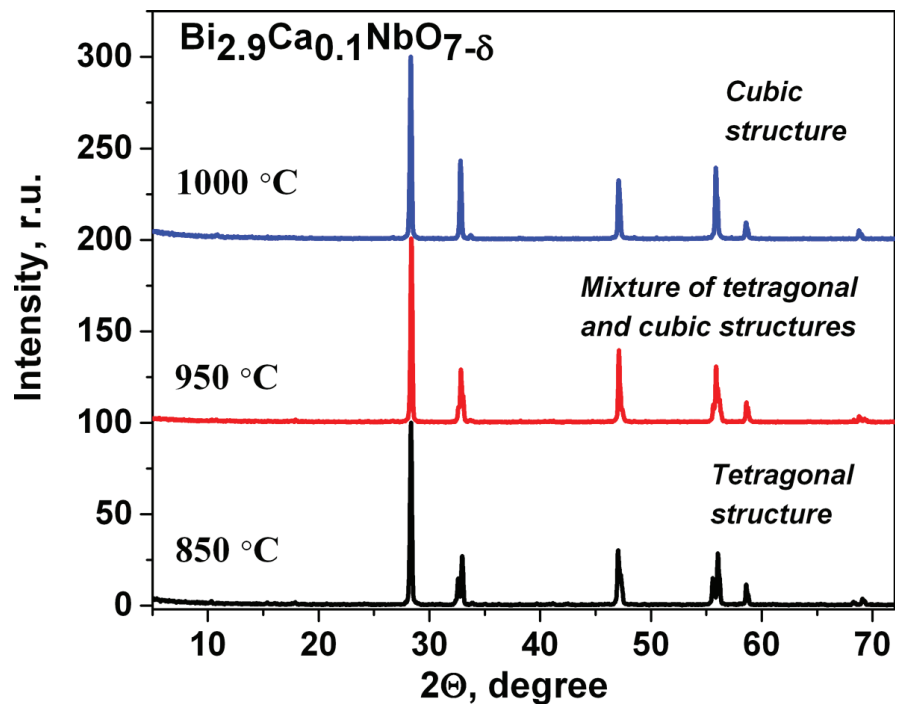
Figure 1: X-ray diffraction patterns of the sample $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ after different synthesis temperatures.

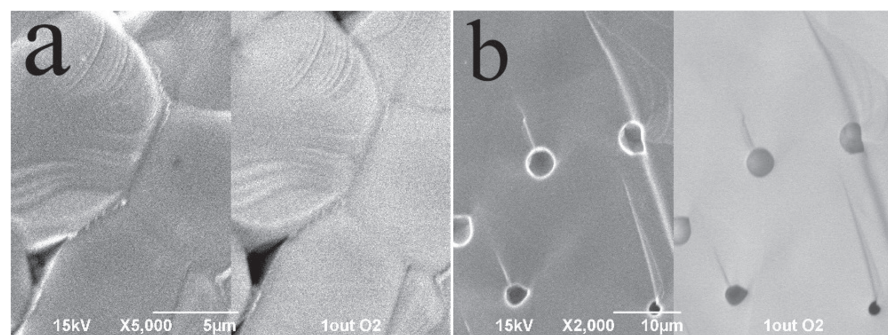**Figure** 2: SEM images of the briquette sample $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ sintered at 1000°C: (a) surface and (b) chip.

taking place both inside and on the phase boundaries. At high temperatures, a speed of charge carriers in the electrolyte volume is sufficiently large for distinguishing separated components (Figure 4(a)). For example, for the sample Bi_3NbO_7 ($T_{Synthesis}$ = 850°C) the value of capacity CPE1 for the equivalent scheme corresponding to the impedance spectra obtained at 825°C is equal to 10^{-5} F. This value relates to electrolyte-electrode contacts and electrochemical reactions on the electrodes. Analyzing in similar way the equivalent scheme for the same sample at 475°C we have found that it can be possible to distinguish a volume and grain boundary resistance at low temperatures. It agrees with the calculated capacity values: 5×10^{-10} F (CPE1) – volume resistivity, 2.5×10^{-7} F (CPE2) and 1.9×10^{-7} F (CPE3) – grain boundary resistivity [9].

TABLE 1: Phase composition of the samples $Bi_{3-x}M_xNbO_{7-\delta}$ (M = Ba, Ca, Mg, or Sr; x = 0, 0.1) at different synthesis temperatures.

T, °C	Nominal Composition	Phase Composition (ICDD PDF 4)	W, %
850	Bi_3NbO_7	$Nb_{16}Bi_{47}O_{111}$	100
	$Bi_{2.9}Ba_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	77
		$BaNb_2Bi_2O_9$	4
		$Nb_{16}Bi_{47}O_{111}$	19
	$Bi_{2.9}Mg_{0.1}NbO_{7-\delta}$	$Nb_{16}Bi_{47}O_{111}$	98
		$Mg_{0.7}Nb_{15.2}Bi_{16.67}O_7$	2
	$Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$	$Nb_{16}Bi_{47}O_{111}$	100
	$Bi_{2.9}Sr_{0.1}NbO_{7-\delta}$	$Nb_{16}Bi_{47}O_{111}$	100
950	$Bi_{2.9}Mg_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	92
		$Mg_{0.7}Nb_{15.2}Bi_{16.67}O_7$	8
	$Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$	$Nb_{16}Bi_{47}O_{111}$	36
		Bi_3NbO_7	64
	$Bi_{2.9}Ba_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	97
		$BaNb_2Bi_2O_9$	2
		$BaNb_{0.5}Bi_{0.5}O_8$	1
	Bi_3NbO_7	Bi_3NbO_7	100
	$Bi_{2.9}Sr_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	94
		$SrNb_2Bi_2O_9$	6
1000	Bi_3NbO_7	Bi_3NbO_7	100
	$Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	100
	$Bi_{2.9}Sr_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	92
		$SrNb_2Bi_2O_9$	8
	$Bi_{2.9}Ba_{0.1}NbO_{7-\delta}$	Bi_3NbO_7	88
		$BaNb_2Bi_2O_9$	12
	$Bi_{2.9}Mg_{0.1}NbO_7$	Bi_3NbO_7	91
		$Mg_{0.7}Nb_{15.2}Bi_{16.67}O_7$	9

Plotted temperature dependences of the electroconductivity (Figure 5) have linear shape almost for all samples with activation energy (E_a) values close to 1 eV. This is related to primary ionic character of the electroconductivity and is in a good agreement with literature data, according to which the Bi_3NbO_7 is an oxide ion conductor [8]. A small anomaly was observed in the form of a slight bend of the curve on -lgσ – 1000/T dependence around 650°C for the $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ with tetragonal structure. The definite reason of this phenomenon has not been determined yet and can be

TABLE 2: The unit cell parameters of the single phase compounds.

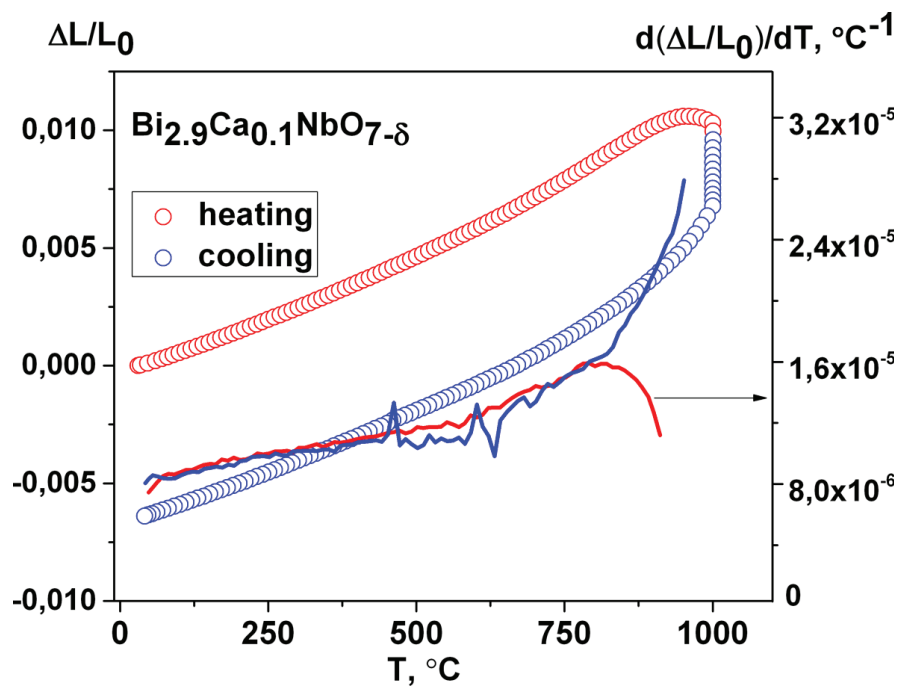| Compound	a ± 0.002, Å	c ± 0.001, Å	V ± 0.05, Å^3
$T_{Synthesis}$ = 850°C: tetragonal structure (S.G. *I-4m2*)			
Bi_3NbO_7	7.783	5.490	324.10
$Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$	7.727	5.651	336.92
$Bi_{2.9}Sr_{0.1}NbO_{7-\delta}$	7.692	5.499	325.18
$T_{Synthesis}$ = 1000°C: cubic structure (S.G. *Fm3m*)			
Bi_3NbO_7	5.461	–	162.78
$Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$	5.459	–	162.63

Figure 3: Temperature dependences of the linear size changes and TEC of $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ with cubic structure.

related either with electroconductivity type changes from intrinsic to impurity conduction at decreasing of temperature measurement or with possible infrastructural changes, which need additional study. The electroconductivity values of the pure bismuth niobate with tetragonal structure are slightly higher than those for the one with cubic structure (Figure 5). Whereas for the doped samples such tendency does not remain. So for the $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ after synthesis at 850°C σ_{750} = 4.9×10^{-4} Ohm^{-1}cm^{-1}, after 1000°C – σ_{750} = 1.1×10^{-3} Ohm^{-1}cm^{-1}. In general, an introduction of alkaline earth elements into bismuth niobate structure did not lead to a significant increase of the electroconductivity values in the mentioned concentration interval in comparison with
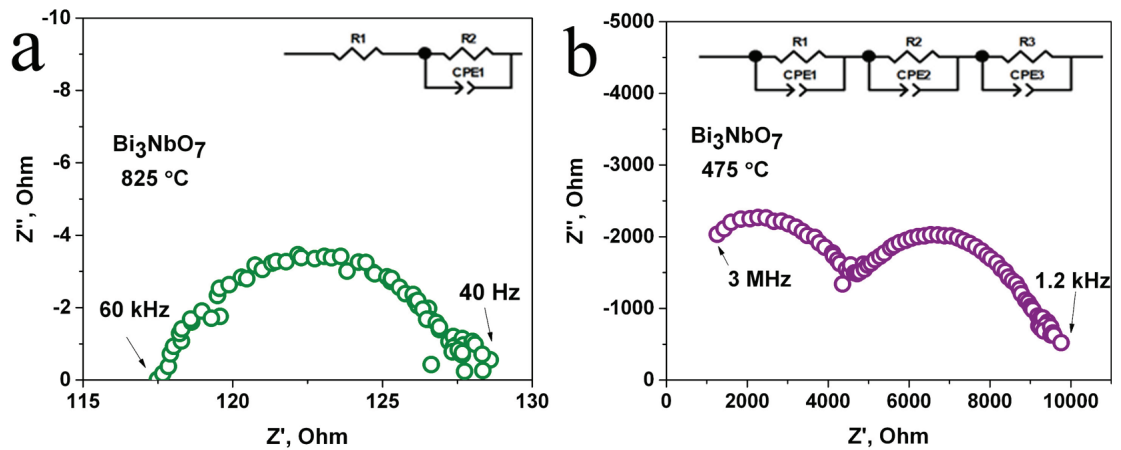
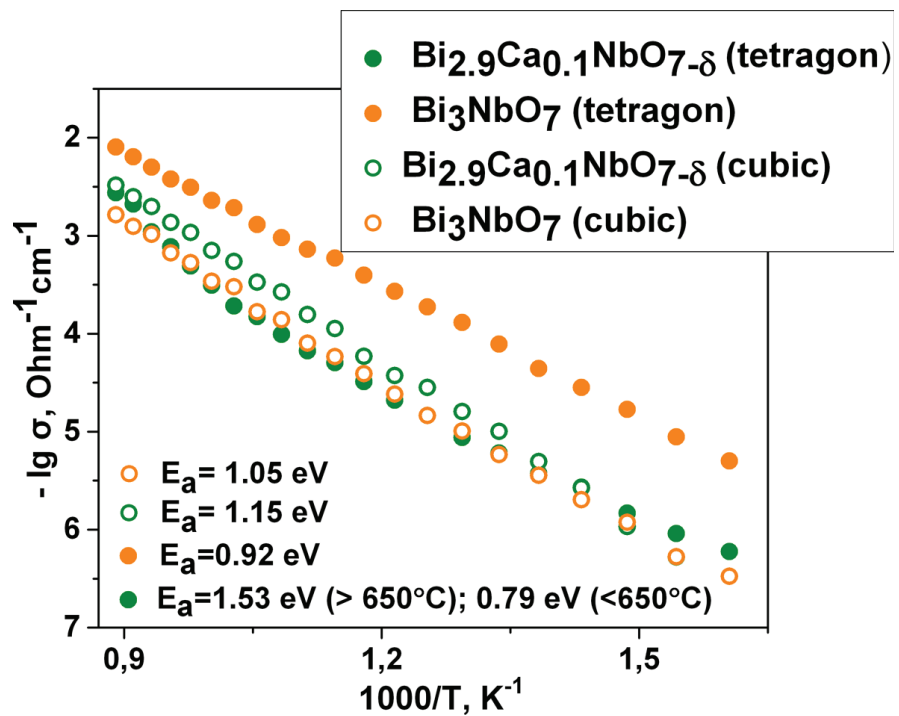**Figure** 4: Impedance spectra $Bi_{2.9}Ca_{0.1}NbO_{7-\delta}$ ($T_{Synthesis}$ = 850°C) obtained at: (a) 825°C and (b) 475°C.

Figure 5: Temperature dependences of the electroconductivity $Bi_{3-x}Ca_xNbO_{7-\delta}$ (x = 0, 0.1) with tetragonal and cubic structure.

the matrix compound. One of the main reasons of such behavior can be low dopant content (2.5 wt.%).

4. Conclusion

The opportunity of generation of the single phase samples of bismuth niobates doped by calcium and strontium was confirmed using solid state synthesis method. Similar to the pure bismuth niobate Bi_3NbO_7, there is a transition from a tetragonal structure

(S. G. *I-4m2*) to a cubic one (S. G. *Fm3m*) in the temperature range 850–1000°C. The dense sintered ceramic specimens were obtained with TEC equal to 10×10^{-6} °C^{-1}. Full phase composition of the samples was determined. The electroconductivity values of the bismuth niobate with a tetragonal structure are higher than those with a cubic one. However, for the calcium doped niobate, the similar tendency does not remain. Further step of our work will be directed to an expansion of a doping concentration interval of the calcium doped bismuth niobate as the most stable and perspective material for more detailed consideration.

Funding

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