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Influence of synthesis method on the properties of mixed Aurivillius phase $Bi_5TiNbWO_{15}$

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Abstract The ceramic material $Bi_5TiNbWO_{15}$ (BTNW) was obtained and is characterized by a layered, Aurivillus type structure *(MBLPO—mixed bismuth oxide layered perovskites)* with m=1.5. In order to optimize the production, BTNW was synthesized by two methods: synthesis of a mixture of simple oxides Bi_2O_3, Nb_2O_5, WO_3, TiO_2 and synthesis of a mixture of appropriate, layered Aurivillus type structures Bi_2WO_6 (m=1) and Bi_3TiNbO_9 (m=2). Synthesized solid solutions were consolidated with a conventional method. The crystal structure of Bi_2WO_6 and Bi_3TiNbO_9 $Bi_5TiNbWO_{15}$ was examined at room temperature with an X-ray diffraction method. Microstructure and chemical composition were analyzed. The authors analyzed the temperature—permittivity ε relationship for the ceramic with m=1,5, which was obtained with two methods, as well as for m=1 and m=2.

Keywords Synthesis · XRD · SEM · Dielectric properties · Ferroelectric properties · Mixed Aurivillius phases

1 Introduction

The Aurivillius type compounds are characterized by a range of unique properties, which are interesting due to their application possibilities. Majority of these compounds display ferroelectric properties at room temperature with Curie point T_c between 300–950°C and melting point at T_{melt}>1100°C. The ceramic materials obtained on the basis of these compounds play a role in many applications, for example, in high temperature piezoelectric transducers of various types; the crystals and thin layers are used as electro-optic modulators, displays, ferroelectric memories, etc. [1–4].

The structure of the Aurivillius phases (BLPO—*bismuth oxide layered perovskites*) is usually described as a result of a regular growth of the bismuth—oxygen $[Bi_2O_2]^{2+}$ and perovskite-like $(A_{m-1}B_mO_{3m+1})^{2-}$ layers. The m number is a natural number, which denotes the quantity of oxygen octahedrons BO_6, which are formed along the c-axis. A—describes locations of ions of the dodecahedral coordination (Ba, Ca, Pb, Sr, Bi, Cd, and others), and B—locations of ions of the octahedral coordination (Nb, Ti, Fe, Ta, and others) [5–8].

It was observed that the growth of the structures of this type was disturbed, i.e., layers with different m values were interwoven. However, it was always a periodical growth of half unit cell with m and m+1 perovskite-like layers. Layers m and m+1 are shifted in relation to the bismuth-oxygen layers by $a_0/\sqrt{2}$ in the [110] direction, where a_0 is a parameter of a regular perovskite cell. Compounds with this type of structure are called mixed Aurivillius phases (MBLPO—*mixed bismuth oxide layered perovskites*) and are described by the following formula: $A_{2m\ and\ 2}Bi_4B_{2m}O_{6m+6}$. $Bi_5TiNbWO_{15}$ (BTNW) is the simplest compound of this type. Its structure, with m=1.5, is formed from interwoven layers of Bi_2WO_6 with m=1 and Bi_3TiNbO_9 with m=2 [9–13].

The formation of the mixed Aurivillius structures displaying ferroelectric properties has not been adequately

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researched either experimentally or theoretically. The production technology of these compounds present substantial problems due to their complex structure.

The purpose of this study was to determine the optimal method of production of the $Bi_5TiNbWO_{15}$ ceramic material. It has been one of the first applications of solid solutions Bi_2WO_6 and Bi_3TiNbO_9 in the BTNW synthesis. Furthermore, the authors analyzed the crystal structure, microstructure, and basic dielectric properties of the BTNW ceramic obtained from both the synthesis of the simple oxides mixture and the synthesis of the mixture of appropriate BLPO. The initial solid BLPO solutions underwent similar analysis with a purpose of finding possible regularities and confirming the existence of a homogeneous BTNW phase.

2 Experimental

The authors designed the production technology of the $Bi_5TiNbWO_{15}$ ceramic characterized by the mixed, layered, perovskite-like structure. The synthesis was carried out by two methods. The first method is a synthesis of a stoichiometric mixture of simple oxides (BTNW-1–$Bi_5TiNbWO_{15}$ obtained by the first method) according to reaction:

$$Bi_2O_3 + TiO_2 + Nb_2O_5 + WO_3 \rightarrow Bi_5TiNbWO_{15} \quad (1)$$

The second method of synthesis included two stages. Initially, the BLPO with $m=1$ and $m'=2$ was obtained according to reaction:

$$Bi_2O_3 + WO_3 \rightarrow Bi_2WO_6 \quad m = 1 \quad (2)$$

$$3Bi_2O_3 + 2TiO_2 + Nb_2O_5 \rightarrow 2Bi_3TiNbO_9 \quad m' = 2\,; \quad (3)$$

Table 1 Conditions of ceramic synthesis and sintering by a conventional method.

Material	Calcination	Sintering	Time	Density
	T_{SI} (°C)	T_{SII} (°C)	t_S (h)	ρ (g/cm^3)
Bi_2WO_6	800	850	3	7.07
Bi_3TiNbO_9	800	1150	3	7.53
BTNW-1	800	1050	3	7.99
BTNW-2	800	1050	3	7.89

Processing conditions used in the process of conventional ceramic sintering

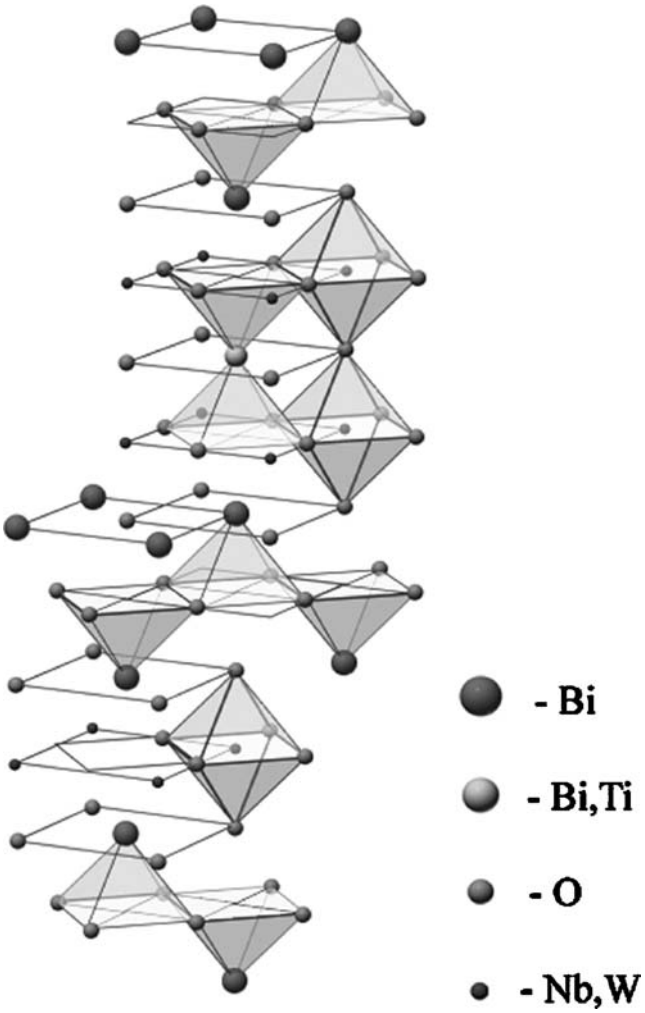

Fig. 1 Prototype structure of $Bi_5TiWNbO_{15}$

subsequently, the $Bi_5TiNbWO_{15}$ (BTNW-2–$Bi_5TiNbWO_{15}$ obtained by the second method), was synthesized from the stoichiometric mixture according to reaction:

$$Bi_2WO_6 + Bi_3TiNbO_9 \rightarrow Bi_5TiNbWO_{15} \quad (4)$$

The ceramic samples were obtained by the conventional method as a result of a reaction in the solid phase. The mixture ingredients were mixed manually for 20 h, and then were calcinated in the air at T_{SI}=800°C for 5 h. The optimal conditions for sintering (Table 1) were determined based on densities of the obtained ceramic samples, analyses of both crystal structure and microstructure, chemical composition and permittivity $\varepsilon(T)$. All ceramic samples used for the analysis of the dielectric properties had a form of a disk with the diameter of 10 mm and thickness of 1 mm. Conducting platinum electrodes were deposited on unpolished, flat surfaces of the samples by cathode sputtering.

The authors examined the crystal structure and phase composition of the ceramic materials by an X-ray diffraction

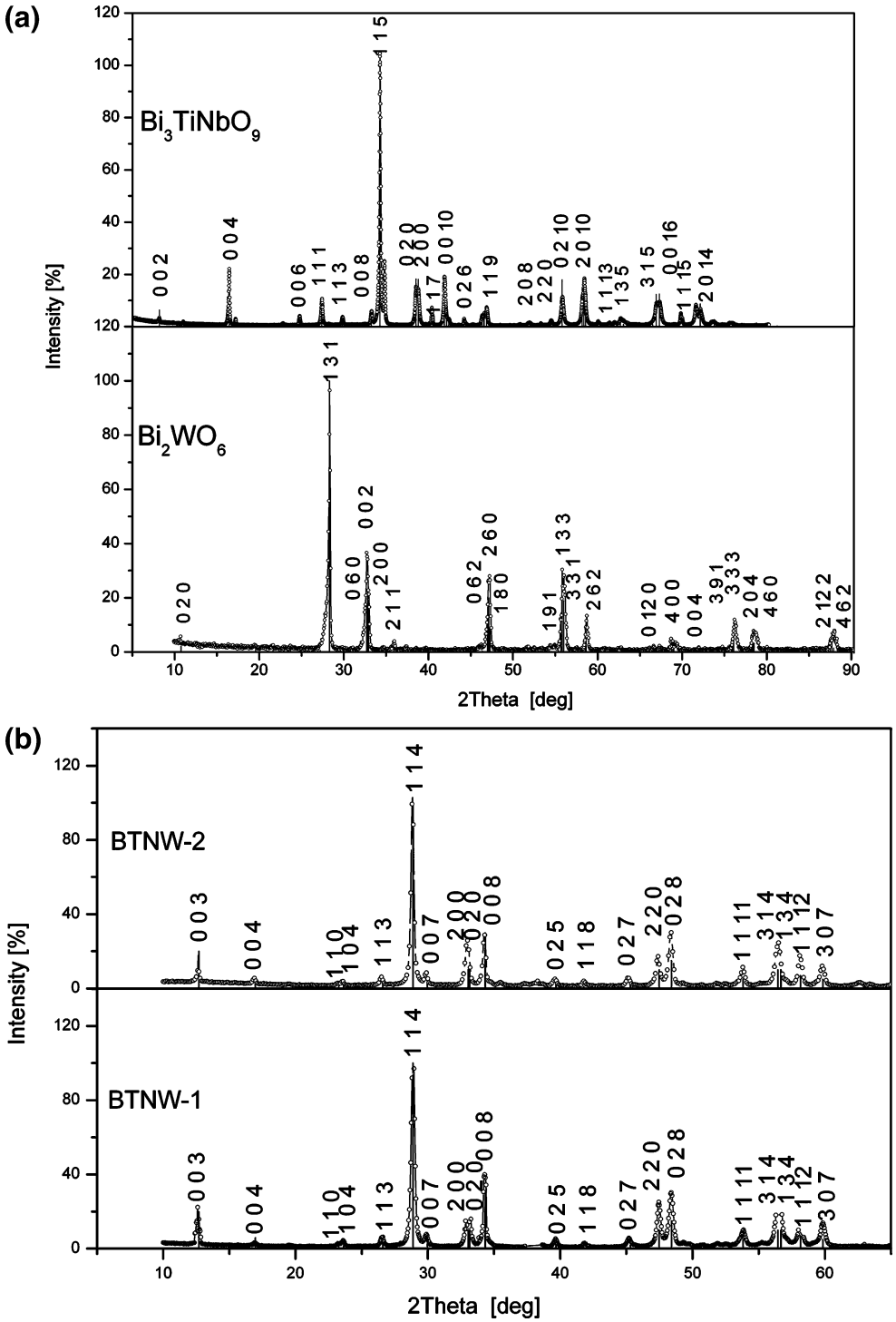

Fig. 2 X-ray diffraction pattern for: (**a**) Bi_2WO_6 and Bi_3TiNbO_9; (**b**) BTNW-1 and BTNW-2

method with an X'Pert—Philips PW 3040/60 diffractometer. The measurements were conducted for the following conditions: radiation of CuKα=1.5418 Å, graphite monochromator, voltage of 40 kV, amperage of 35 mA, impulse count rate of 2 seconds, and the counter shift rate of 0.020.

The microstructure of the ceramic was analyzed with a scanning electron microscope HITACHI S-4700 with an analytic attachment EDS with a magnification of 5000. The authors conducted microstructural analysis and an investigated the EDS chemical composition of the ceramic. The research conducted with the electron microscope included: representation of morphologies and surfaces of tested samples as well as qualitative and quantitative analysis of chemical composition in micro areas.

Table 2 List of unit cell parameters.

Material	From *ICDD* Card			Experimental		
	(nm)			(nm)		
	a_0	b_0	c_0	a_0	b_0	c_0
Bi_2WO_6	0.5437	0.5458	1.6430	0.5427±0.0009	0.5475±0.0009	1.6460±0.0016
Bi_3TiNbO_9	0.5405	0.5420	2.5110	0.5397±0.0008	0.5447±0.0009	2.5149±0.0018
BTNW-1	0.5415	0.5410	2.0890	0.5412±0.0005	0.5407±0.0005	2.0897±0.0015
BTNW-2				0.5418±0.0004	0.5417±0.0006	2.0941±0.0019

The analyses of the temperature–permittivity (ε) relationship were conducted at the frequency of 20 kHz and temperature range not exceeding 1,000°C with a Quadtech 1920 impedance meter.

3 Results

Regardless of the synthesis method, the crystallization process of the BTNW solid solution results in formation of perovskite layers along the *c*-axis. The layers, with the WO_4^{3-} composition, are one octahedron thick and are interwoven with other perovskite layers, which are two octahedrons thick. These layers are separated by the bismuth-oxygen layers $(Bi_2O_2)^{2+}$ (Fig. 1). The $Bi_5TiNbWO_{15}$ structure can be treated as a structure composed of a half unit cell $[(Bi_2O_2)^{2+}(WO_4)^{3-}]$ with $m=1$ (Bi_2WO_6) and a half unit cell $[(Bi_2O_2)^{2+}(BiNbTiO_7)^{-}]$ with $m'=2$ (Bi_3TiNbO_9).

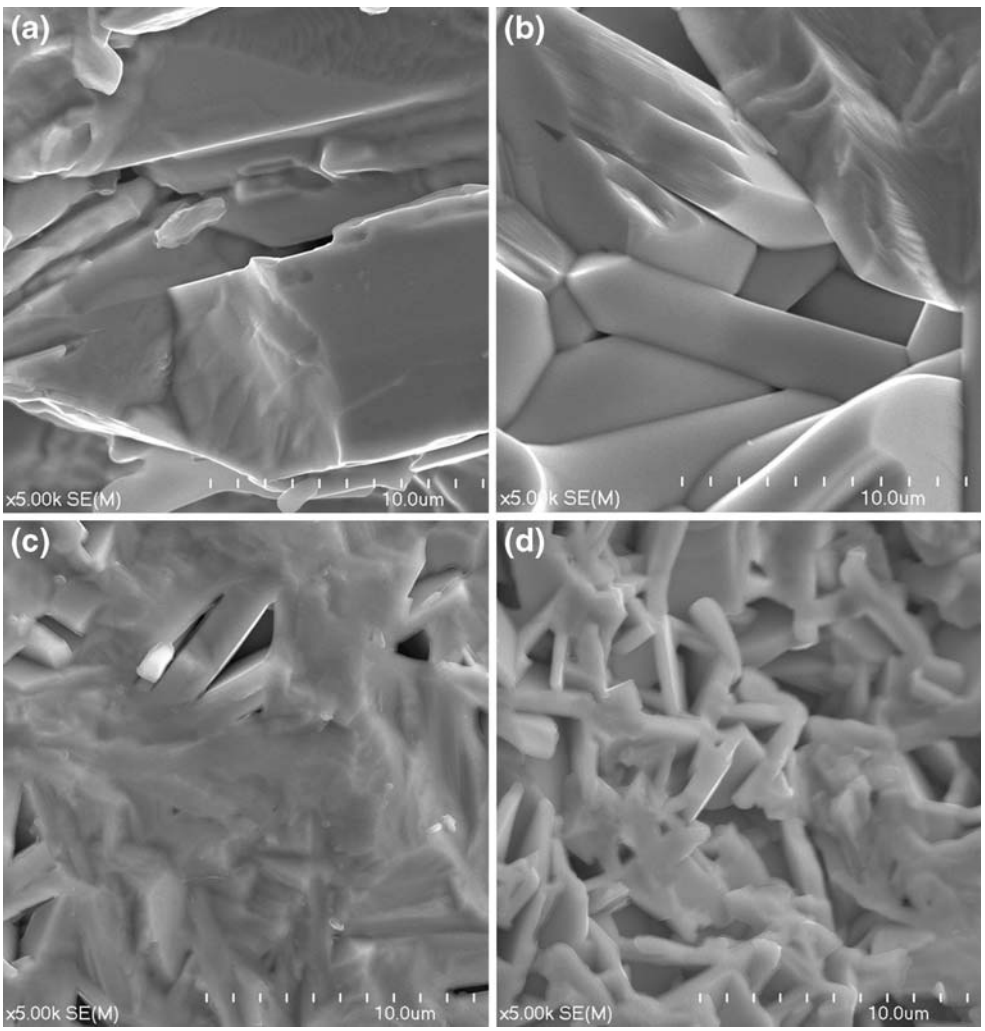

Fig. 3 Microphotographs of ceramic sample surfaces obtained by the conventional method for the ceramic with the following *m* values: (**a**) 1; (**b**) 2; (**c**) 1.5 BTNW-1; (**d**) 1.5 BTNW-2

Table 3 Results of analysis of chemical composition EDS.

Oxides	Chemical composition of ceramics (%)			
	Bi_2WO_6	Bi_3TiNbO_9	BTNW-1	BTNW-1
Bi_2O_3	65.74±2	74.01±2	68.87±2	68.39±2
WO_3	35.26±1	–	16.91±1	17.15±1
TiO_2	–	10.34±1	5.42±1	5.51±1
Nb_2O_5	–	15.65±1	9.40±1	10.05±1

EDS Analysis

The results of analysis of the crystal structure of Bi_2WO_6 (a), Bi_3TiNbO_9 (a), BTNW-1 (b), BTNW-2 (b) are schematically presented on Fig. 2. The obtained X-ray diffraction pattern were compared with models from the ICDD international data basis (model 31-0203 for BTNW-1 and BTNW-2; model 79-2381 for Bi_2WO_6; model 73-2180 for Bi_3TiNbO_9), which confirmed the occurrence of single-phase arrangement in each obtained solid solution. Values of a_0, b_0, and c_0 were optimized by a method of least squares in the *UnitCell* program using a full spectrum of experimental diffraction maximums.

The obtained results were listed together with the standard values (Table 2). The Bi_2WO_6 material is characterized by a rhombic structure with a -*Pca21* space group and the following parameters of a unit cell: a_0= 0,5427 nm, b_0=0.5475 nm, and c_0=1.6460 nm. The Bi_3TiNbO_9 material also has a rhombic structure with the -*Pccn* space group and the following lattice parameters: a_0=0.5397 nm, b_0=0.5447 nm, and c_0=2.5149 nm (Fig. 2(a)). The X-ray diffraction pattern of $Bi_5TiNbWO_{15}$ (Fig. 2(b)) displays diffraction lines with deflection angles 2Θ similar to the 031-0203 model. The BTNW-1 structure was identified as a rhombic arrangement with the following dimensions of a unit cell: a_0=0.5412 nm, b_0=0.5407 nm, and c_0=2.0897 nm; in the case of BTNW-2 - a_0=0.5418 nm, b_0=0.5417 nm, and c_0=2.0941 nm. (Fig. 2(b)). A significant increase of the c_0 parameter with increasing number of layers m was observed in the structures of the obtained compounds, which is typical for the Aurivillius structures. The widening and displacement of some diffraction lines in BTNW-1 and BTNW-2 (e.g. *hkl* reflections: 200, 020, 008, and 220) are most probably caused by deviations of the ideal periodic lattice, such as: internal stresses, dislocations etc.

Figure 3(a), (b), and (c) present results of microstructural analyses. The scaly structure, which is typical for the layered structure, was observed in all cases. Scales are irregularly oriented in relation to one another and have an appearance of built up plates. The $Bi_5TiNbWO_3$ ceramic material has a structure of chaotically oriented grains with angular faces of the scaly and needle-like habit. The microstructure of BTNW-1 and BTNW-2 displays, above all, grains with the length of l <5 μm. The BTNW-2 microstructure is characterized by greater porosity. Microstructure of Bi_2WO_6 and Bi_3TiNbO_9 is a mosaic of flaky grains (the length of l <10 μm), which are heterogeneous in respect to their size.

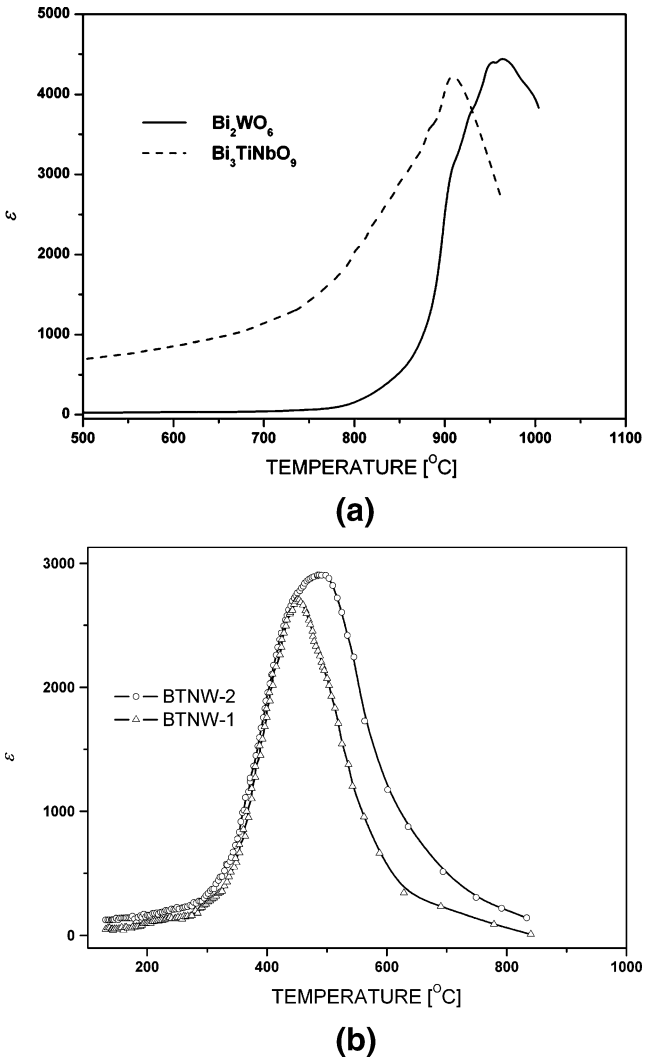

Fig. 4 Dependence of permittivity (ε) on temperature (T) for the following ceramic materials: (**a**) Bi_2WO_6 and Bi_3TiNbO_9; (**b**) BTNW-1 and BTNW-2

Table 4 Dielectric properties of the obtained ceramic materials.

Material	ε_{RT}	T_m (°C)	ε_m
Bi_2WO_6	7	980	4480
Bi_3TiNbO_9	105	900	4220
BTNW-1	89	455	2703
BTNW-2	92	493	2924

Comparison of dielectric parameters for layer type bismuth ceramics

Analyses of the chemical composition confirmed the concentrations of individual elements in the solid solutions according to the stoichiometry (Table 3).

Figure 4 presents a permittivity ε –temperature relationship for: (a) Bi_2WO_6 and Bi_3TiNbO_9 as well as (b) BTNW-1 and BTNW-2. It was noted that all examined ceramic materials are characterized with a phase transition that occurs at high temperatures.

For Bi_2WO_6 the permittivity reaches the maximal value at 980°C and for Bi_3TiNbO_9—at 900°C (Fig. 4(a)) confirming the ferroelectric-paraelectric transition, which occurs in these compounds For the BTNW-2 ceramic, the graph displays a wide maximum on the ε curve at 450–520°C and for the BTNW-1 ceramic—at 430–480°C (Fig. 4(b)). For the BTNW-2, the dielectric constant reaches the value of ε=2924 at 493°C, while for the BTNW-1, its value is significantly lower and at 455°C equals ε=2703. Table 4 presents the values of dielectric constant for the BLPO ceramic material with m=1 and m=2, and for the MBLPO with m=1.5. The differences in permittivity and phase transition temperature for BTNW-1 and BTNW-2 could be caused by greater porosity of BTNW-2 and greater depth of electrode penetration. Strong ionic conductivity of the bismuth-oxygen ions may also be highly important. Probably, due to this fact, the non-linear (hysteresis loop) and piezoelectric properties were not observed.

4 Conclusions

The authors design a technology of production of a ceramic with mixed layered Aurivillius structure of the $A_{2m-2}Bi_4B_{2m}O_{6m+6}$ type (with m=1.5). Ferroelectric ceramic $Bi_5TiNbWO_{15}$ can be obtained from the synthesis of simple oxygen mixtures and the synthesis of appropriate BLPO (Bi_2WO_6, Bi_3TiNbO_9) mixtures. The X-ray analysis of BTNW-1 and BTNW-2 demonstrated that the obtained ceramics have a single phase (no phase reflections: Bi_2WO_6 or Bi_3TiNbO_9) and are characterized with a crystal structure, which is in conformity with the *ICDD* models. The c_0 parameters of a unit cell of the $Bi_5TiNbWO_{15}$ have intermediate values in relation to the values for BLPO with m=1 and m=2. At room temperature, Bi_2WO_6 and Bi_3TiNbO_9 display rhombic structure, while BTNW-1 and BTNW-2—orthorhombic.

The authors found that the synthesis method had an impact on microstructure (greater porosity of BTNW-2) and dielectric properties (different values of permittivity ε and temperature of phase transition for $Bi_5TiNbWO_{15}$). The ferroelectric properties of all three compounds are demonstrated by the permittivity ε versus temperature graphs $\varepsilon(T)$. The method of synthesis influenced on value of transition temperature and dielectric permittivity for BTNW-1 and BTNW-2.

None of the compounds displays nonlinear properties (electric hysteresis $P(E)$) and was permanently polarized even though various methods and conditions of polarization have been applied. Absence of experimental manifestations of ferroelectric state, such as loop of electric hysteresis, and piezoelectric properties can be related to a low quality of the microstructure of ceramic compounds, which is characteristic for the Aurivillus structures, and relatively high electrical conductivity. The authors believe that improvement these parameters (microstructure, ferroelectric properties and conductivity) is possible to get by use different method of obtaining, for example: HUP or HF methods.

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