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STUDIES OF TEMPERATURE AND FABRICATION METHODS INFLUENCE ON STRUCTURE AND MICROSTRUCTURE OF BiNbO_4 MICROWAVE ELECTROCERAMICS

BADANIA WPŁYWU TEMPERATURY I PROCESU WYTWARZANIA NA STRUKTURĘ ORAZ MIKROSTRUKTURĘ MIKROFALOWEJ CERAMIKI BiNbO_4

The bismuth-based ceramics are well known as potential materials for microwave or microelectronics applications. One of them is a bismuth niobate (BiNbO_4), which belongs to the family of the scheelite-like stibiotantalite structure $\text{A}^{3+}\text{B}^{5+}\text{O}_4$. This low temperature co-fired dielectric ceramics is also reported as a good microwave dielectric material, using i.e. in multilayer microwaves systems.

In the present studies depends of fabrication methods and temperature conditions on basic properties of bulk BiNbO_4 are reported. Technological process included two stages. First, the ceramic powder was obtained from the high purity oxides (99.99%), by MOM method. The second stage involved consolidation of such prepared powders by free sintering and the hot uniaxial pressing methods. Goal of this study was to investigate how the fabrication processes i.e. temperature and sintering conditions influence on prepared powders and samples of bismuth niobate, like its structure and microstructure.

Keywords: Bismuth niobate, scheelite-like structure, microwave ceramics

Ceramika na bazie bizmutu znana jest jako potencjalny materiał do zastosowań w technice mikrofalowej oraz mikroelektronice. Jednym z jej przedstawicieli jest niobian bizmutu (BiNbO_4), który należy do rodziny związków o strukturze szelito podobnej, tantalanu antymonu $\text{A}^{3+}\text{B}^{5+}\text{O}_4$. Ceramika dielektryczna tego typu, wypalana niskotemperaturowo, przedstawiana jest również jako materiał o dobrych właściwościach mikrofalowych, wykorzystywany np.: w wielowarstwowych układach mikrofalowych.

W przedstawionej pracy omówiono wpływ stosowanych metod wytwarzania oraz ich warunków temperaturowych, na podstawowe właściwości ceramiki BiNbO_4 . Proces technologiczny składał się z dwóch etapów. W pierwszym z nich, techniką MOM otrzymano proszki ceramiczne z wysokiej czystości tlenków (99.99%). Drugi etap obejmował zagęszczanie przygotowanych proszków za pomocą metod spiekania swobodnego i jednoosiowego prasowania na gorąco. Celem pracy było zbadanie wpływu procesu wytwarzania, tzn. temperatury i metod spiekania na otrzymane proszki oraz próbki ceramiczne BiNbO_4 , na ich strukturę oraz mikrostrukturę.

1. Introduction

The significant increase in application of microwave dielectrics as the mobile communications system was observed during last two decade. Miniaturization of passive microwave devices is usual performed using multilayer ceramic technology. In this case green ceramics tapes of different materials corresponding to different passive functions are laminated and co-fired at low temperatures. Unfortunately, most of microwave ceramics can be sintered only at very high temperatures (usual above 1400°C), therefore developing of alternative low co-fired materials becomes important for this technology [1-3].

Bismuth – based dielectrics are well known as low-firing ceramics and have been studied as promising materials for variety applications with respect to the microelectronic industry [4]. One of them is bismuth niobate (BiNbO_4), exhibiting promising microwave properties, i.e. the temperature coefficient of resonant frequency $\text{TCF} \sim 50 \times 10^{-6}/^\circ\text{C}$, the dielectric constant $\epsilon \sim 45$, quality values $Q \sim 4000$ @2GHz, as well relatively lower melting point [5]. BiNbO_4 belong to the bismutocolumbite oxides with similarly to scheelite-like stibiotantalite structure (SbTaO_4) $\text{A}^{3+}\text{B}^{5+}\text{O}_4$. Such low firing materials show a crystal orthorhombic structure (α) in 900°C (Fig.1a) which can be transformed into

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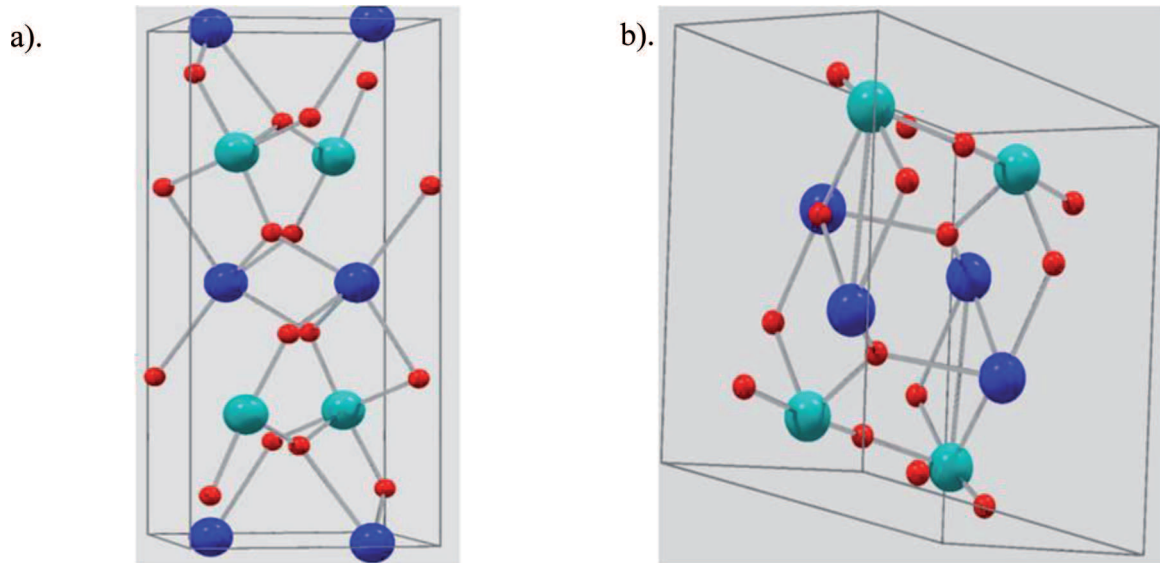


Fig. 1. Models of the scheelite-like stibiotantalite crystal structure of BiNbO_4 , for a) low-temperature orthorhombic α -phase; b) high-temperature triclinic β -phase

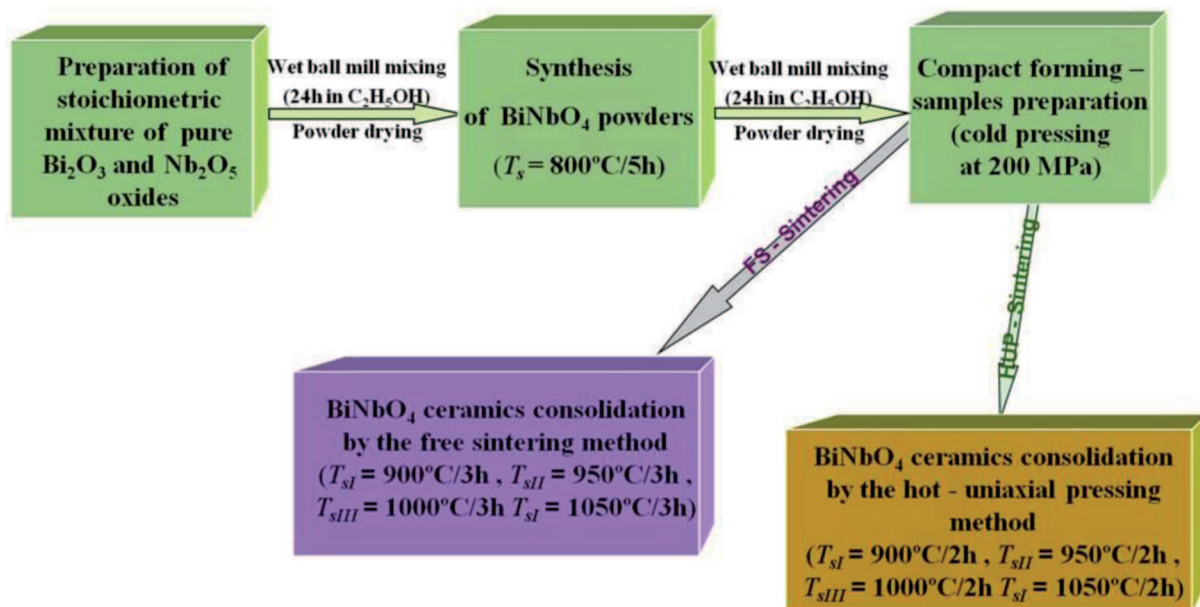


Fig. 2. The flow chart of fabrication process of BiNbO_4 ceramics

a triclinic phase (β), when the sintering temperature is increased above 1020°C (Fig.1b) [6]. Bismuth niobate ceramics with an α -phase are worldwide investigated microwave materials, whereas β - BiNbO_4 ceramics are still not well known materials, probably due to the evaporation of Bi_2O_3 during the high-temperature sintering [7].

The goal of this work was to synthesize BiNbO_4 ceramic powders by the conventional mixed oxide method (MOM) and investigate the influence of different conditions, i.e. temperature and sintering methods on structure and microstructure of bismuth niobate ceramics.

2. Experimental procedure

Fabrication process of BiNbO_4 was performed in solid state reaction, according to equation (1)



The flow chart of the complete fabrication process is shown in Figure 2. Bi_2O_3 and Nb_2O_5 compounds with high purity $>99.99\%$ and in stoichiometric quantities were used to synthesis bismuth niobate powders. Firstly, they were grounded in the mortar, than mixed in the planetary ball mill ($t=24\text{h}$), with small amount of dis-

tilled water and $ZrO_2\text{-}Y_2O_3$ as grinding balls. The reactions of the uncalcined $BiNbO_4$ powders were investigated by differential thermal analysis (DTA) (NETZSCH Geratebau Thermal Analysis STA 409) using a heating rate of $10^\circ\text{C min}^{-1}$ in air from room temperature up to 1300°C . Calcined powders were subsequently examined by X-ray diffraction (XRD; Philips PW 3710), using CuK_α radiation at room temperature, to identify the phases formed and calcination conditions for the fabrication of scheelite-like $BiNbO_4$ powder. Powder morphologies and grain sizes were directly imaged using scanning electron microscopy (SEM; HITACHI S-4700 with system of microanalysis EDS-NORAN Vantage).

The slurry was separated from the grinding media by means of a sieve, and then the powder was completely dried in an air atmosphere and then sintered at $T_s = 800^\circ\text{C}$ for 4h. The calcined powders were mixed again (in the same condition) and then cold pressed into pellets ($\phi = 10\text{mm}$, $p=200\text{ MPa}$). $BiNbO_4$ ceramics were consolidated by both free sintering (FS) and hot uniaxial pressing (HUP) methods, at four different conditions of sintering temperature: $T_{sI} = 900^\circ\text{C}$; $T_{sII} = 950^\circ\text{C}$; $T_{sI} = 1000^\circ\text{C}$; $T_{sI} = 1050^\circ\text{C}$; soaking time $t_{FS} = 3\text{h}$, $t_{HUP} = 2\text{h}$.

Influence of sintering temperature and a method of sintering on density structure and microstructure of bulk $BiNbO_4$ samples was examined using SEM and XRD technique.

3. Results and discussion

A DTA curve obtained for the stoichiometric mixture of Bi_2O_3 and Nb_2O_5 powders is shown in Fig. 3. One can see three endothermic peaks are observed in the DTA curve, in the temperature range $T = 195^\circ\text{C}$, $T = 1069^\circ\text{C}$ and $T = 1233^\circ\text{C}$. Comparing it to results reported previously [8], where DTA analysis was carried out on the same measuring equipment and on the same kind of raw powders, the observed phenomena showed only the phase transition processes, other than for pure Bi_2O_3 or Nb_2O_5 components. The first peak centered at $T = 195^\circ\text{C}$, due to very small mass fluctuation ($TG\sim 0,1\%$) and showed about evaporation of some by-products. The second endothermic peak centered at $T = 1069^\circ\text{C}$ could be caused by the melting of ceramics, when the last peak ($@T = 1233^\circ\text{C}$) may be caused by the material decomposition. It should be noted that very small mass change effects occur at all temperature range ($<0.5\%$).

X-ray diffraction patterns and SEM micrographs (10000x) of $Bi_2O_3+Nb_2O_5$ mixture powders are presented in Fig. 4 and shows only typical lines for pure oxide components. In case of EDS analysis, qualitative chemical composition of the mixed material was revealed (Fig. 5).

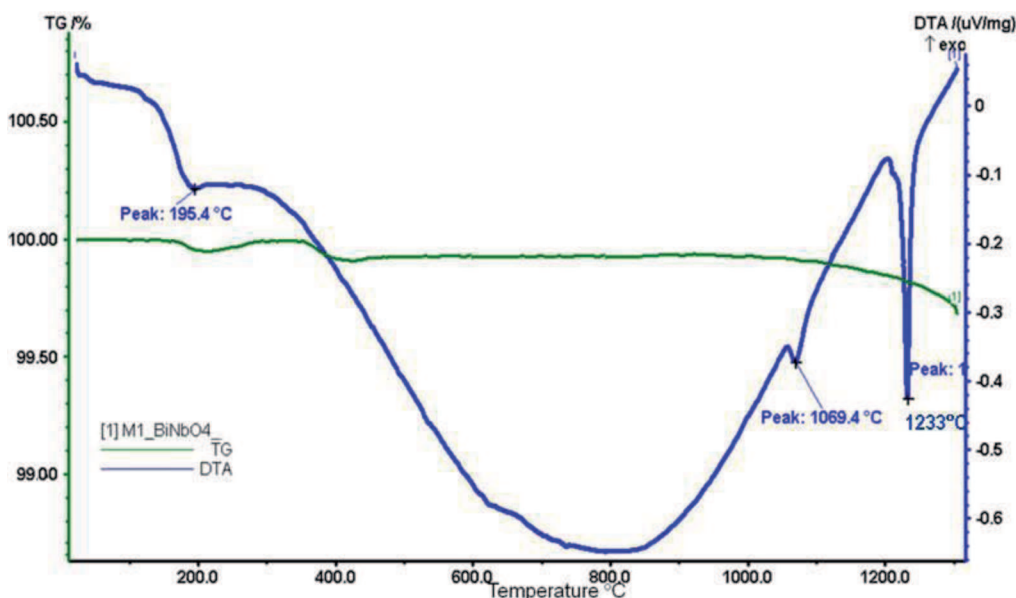


Fig. 3. A DTA curve for the oxides mixture of Bi_2O_3 and Nb_2O_5

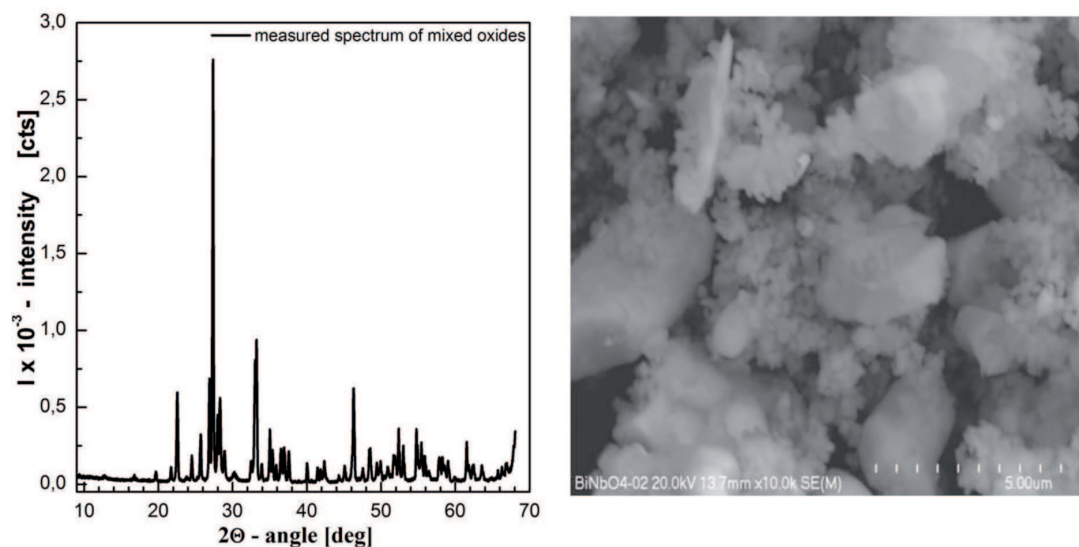


Fig. 4. Typical XRD patterns and SEM micrographs (10000x) of the $\text{Bi}_2\text{O}_3+\text{Nb}_2\text{O}_5$ mixture

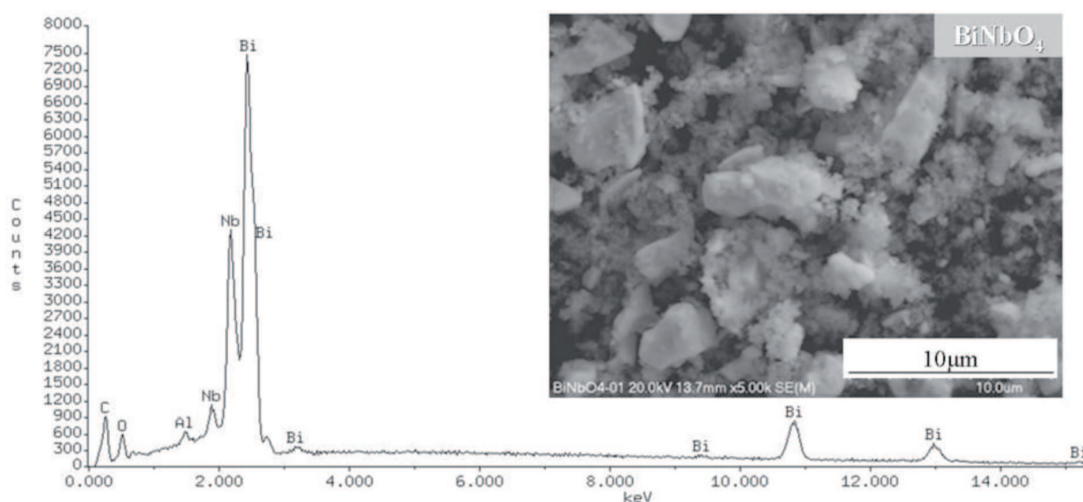


Fig. 5. EDS and SEM micrograph (5000x) of the $\text{Bi}_2\text{O}_3+\text{Nb}_2\text{O}_5$ mixture

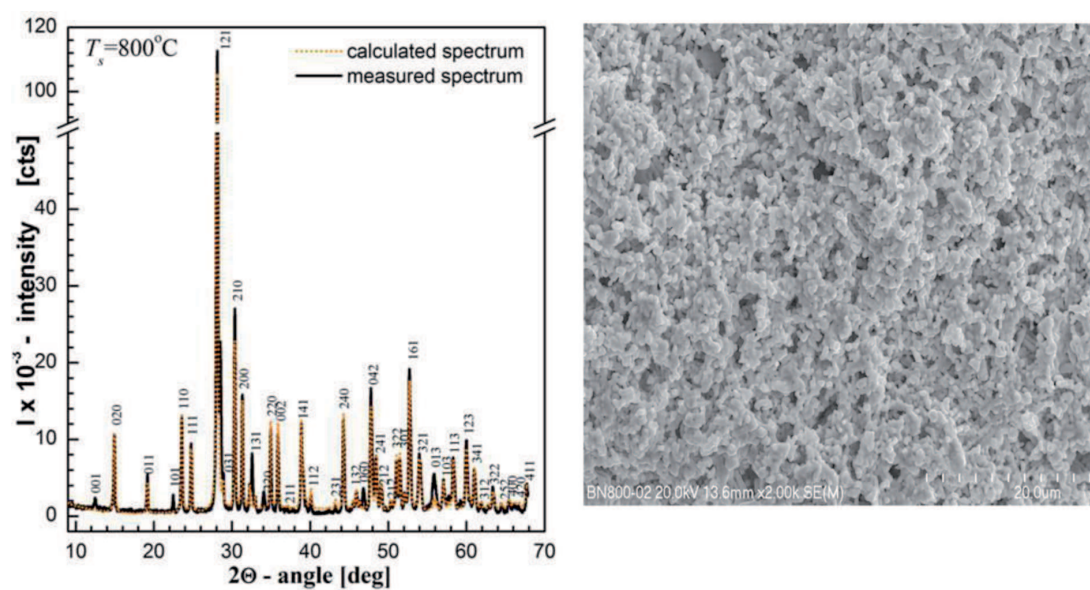


Fig. 6. X-ray diffraction patterns and the SEM micrographs (2000x) of BiNbO_4 , after synthesis ($T_s = 800^\circ\text{C}/5\text{h}$)

The Rietveld refinement method, fixed into X'Pert High Score (Panalytical, B.V) computer programme was used for calculating of the elementary cell parameters. For the diffraction pattern fitting a structure model from ICDD data base was used (PDF standard, nr 00-082-0348).

It was found that the calcined ($T_s=800^\circ\text{C}$) BiNbO_4 sample (Fig.6) exhibited already orthorhombic phase group $Pnna$, with the unit cell parameters: $a_0=5.6720 \text{ \AA}$, $c_0=4.9730 \text{ \AA}$, $V=330.00 \text{ \AA}^3$ and parameters of Rietveld fitting: $R_p=31.56$, $R_{wp}=42.37$, $R_{exp}=0.36$.

Results of the X-ray phase analysis of sintered BiNbO_4 ceramics have indicated that phase transformation had occurred, as a function of sintering temperature.

Also in this case, the Rietveld refinement method has been used for calculating of the elementary cell parameters. All of them, as elementary cell parameters a_0, b_0, c_0 , volume of the elementary cell (V), as well values of the Rietveld R -factors prove a good quality of the fitting process (Table 1). After sintering at temperatures $T_{SI} - T_{SIV}=900\text{-}1000^\circ\text{C}$, the samples exhibited single orthorhombic-type BiNbO_4 phase, irrespective of the FS and HUP sintering method. Temperatures of processes do not influence much on a change of the crystallographic parameters of BiNbO_4 ceramics. Also the influence of the processing method on elementary cell volume was rather small. Only an increase in sintering temperature to $T_{IV}=1050^\circ\text{C}$ caused transformation to triclinic phase as well a small decrease in the crystallographic parameters and elementary cell volume. Thermal evolution of all analyzed X-ray diffraction patterns of FS (A) and HUP (B) sintered BiNbO_4 ceramics are shown in Fig. 7.

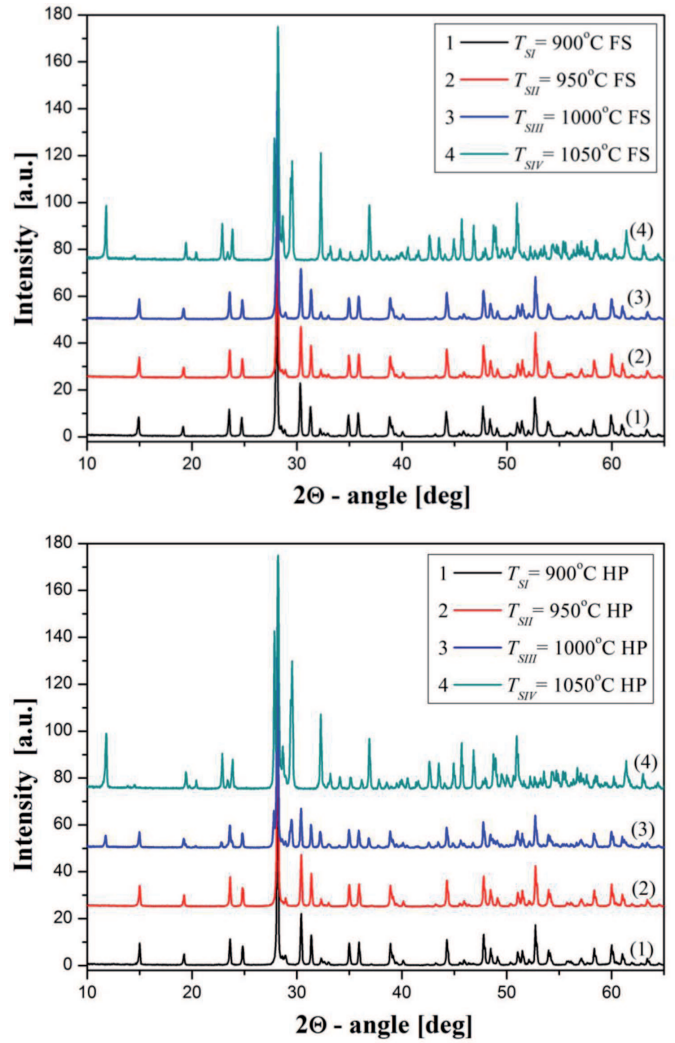


Fig. 7. Thermal evolution of X-ray diffraction patterns of FS (A) and HUP (B) sintered BiNbO_4 ceramics

TABLE 1

The lattice parameters of Rietveld fitting, obtained for BiNbO_4 ceramics consolidated by FS and HUP methods: diffraction pattern fitting factors: R_p – primary, R_{wp} – weighted, R_{exp} – experimental; a_0 [Å], b_0 [Å], c_0 [Å] – parameters of unit cell; V – unit cell volume

BiNbO ₄ SAMPLES T_s [°C]		FITTING FACTORS			SPACE GROUP	CRYSTAL SYSTEM	a_0 [Å]	b_0 [Å]	c_0 [Å]	V [Å ³]
		R_p	R_{wp}	R_{exp}						
FS CERAMICS	900	4.18	55.07	0.49	$52 s.1; Pnna$	orthorhombic	5.674	11.679	4.970	331.9
	950	17.39	25.14	0.51	$52 s.1; Pnna$	orthorhombic	5.677	11.708	4.982	331.9
	1000	16.23	22.94	0.55	$52 s.1; Pnna$	orthorhombic	5.676	11.702	4.979	331.9
	1050	21.63	29.90	1.16	$2s.2; P-1$	triclinic	5.537	7.616	7.929	326.2
HUP CERAMICS	900	28.7	38.41	0.98	$52 s.1; Pnna$	orthorhombic	5.677	11.702	4.977	331.9
	950	16.79	23.71	0.56	$52 s.1; Pnna$	orthorhombic	5.676	11.701	4.978	330.6
	1000	31.59	43.48	1.05	$52 s.1; Pnna$	orthorhombic	5.676	11.703	4.979	330.8
	1050	18.33	25.13	0.64	$2s.2; P-1$	triclinic	5.536	7.614	7.925	326.2

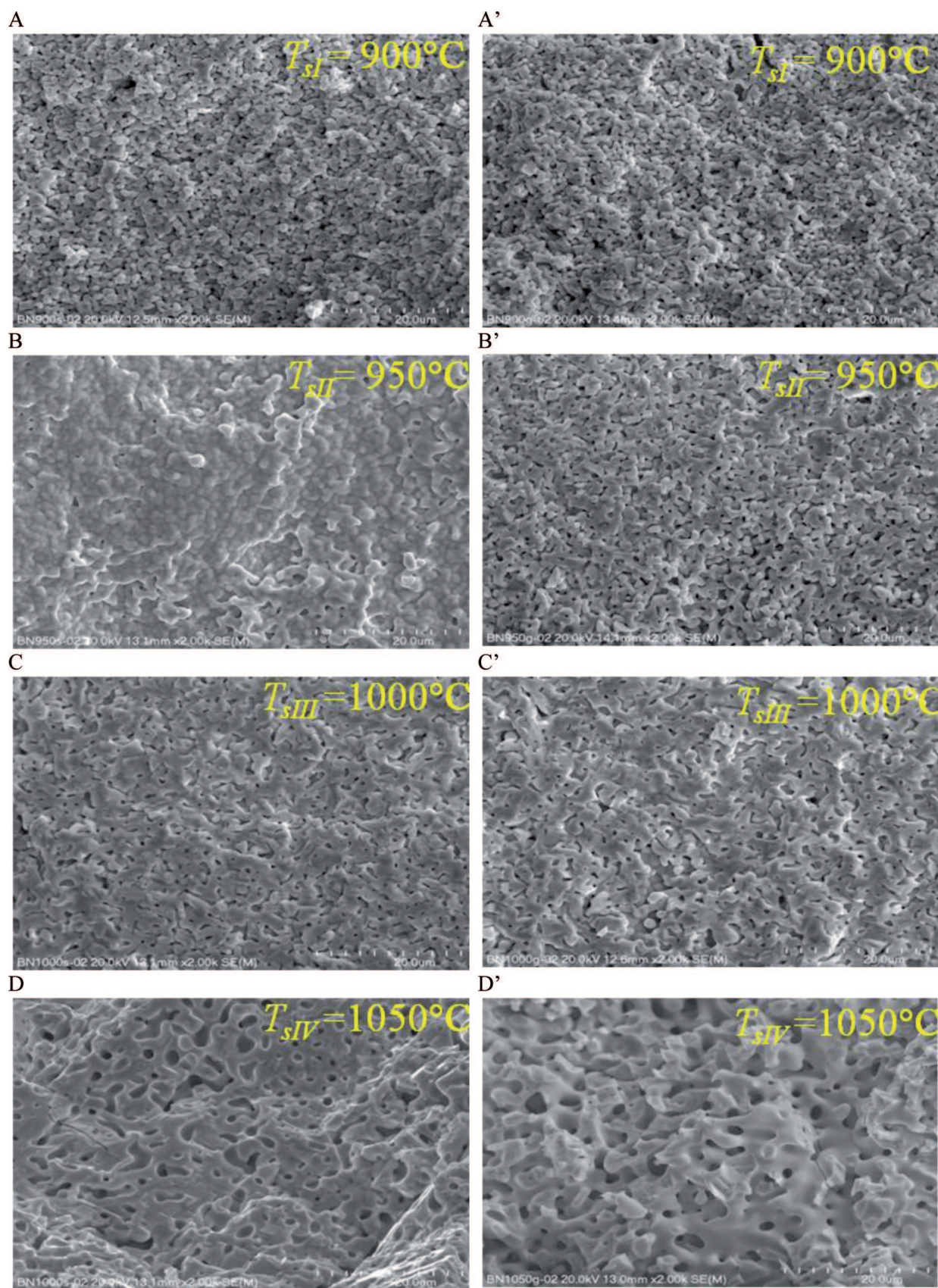


Fig. 8. SEM micrographs of sintered in different temperature FS (A-D) and HUP (A'-D') BiNbO₄ ceramics (2000x)

As is shown at Table 2, in case of all samples obtained by the free sintering method, very low density was measured in comparison to the calculated values. The higher value of relative density $\sim 74\%$ was observed only for samples sintered in $T_{SIII} = 1000^\circ\text{C}$. Fabrication process performed by the hot uniaxial pressing lead to better results of consolidation, but still not fully satisfactory. Also in this case, the highest density showed material sintered at T_{SIII} .

TABLE 2
Value of calculated – $\sigma_{\text{theoretical}}$ and apparent – σ_{exp} density of BiNbO₄ ceramics

BiNbO ₄ SAMPLES $T_s [^\circ\text{C}]$		$\sigma_{\text{theoretical}}$ [kg]	σ_{exp} [kg]	$\sigma_{\text{exp}}/\sigma_{\text{theoretical}} \times 100\%$
Synthesis	800	7364	4683	63.59
FS CERAMICS	900	7321	4440	60.65
	950	7321	4481	61.21
	1000	7321	5416	73.98
	1050	7450	5469	73.41
HUP CERAMICS	900	7321	5067	69.21
	950	7351	5529	75.21
	1000	7321	5947	81.23
	1050	7450	5522	74.12

Analysis of SEM pictures (Fig.8) revealed changes in the morphology of BiNbO₄ ceramics. In case of $T_{SI} = 900^\circ\text{C}$ sintering temperature, pores were easily observed in the cross section of obtained samples (Fig.8.A, A'), regardless if whether FS or HUP method was used. An increase in sintering temperature to $T_{SII} = 950^\circ\text{C}$, definitely improved the packing of the grains in the free sintered samples (Fig.8.B) as compared to the hot-pressed sample. The growth of grain size was observed, but also substantial porosity throughout the sample volume (Fig.8B') did. Subsequent increase in temperature T_{SIII} caused a further growth of grain size for both types of samples. However, this process didn't reduce the grade of porosity but was resulted in partial melting of the sintered material. Further increase in sintering temperature (T_{IV}) caused to complete melting of ceramics, and in high porosity of materials, irrespective of applied consolidation method (Fig.8. D, D').

4. Conclusions

In the present study an influence of different sintering conditions and sintering method on structure and microstructure of BiNbO₄ microwave electroceramics were investigated. Analyses have shown transformation of lattice structure from orthorhombic to triclinic phase, with the increasing in sintering temperature from T_{SI} to T_{SII} , as it was expected. The best result was observed for ceramics sintered by FS method for $T_{SI} = 950^\circ\text{C}$. It was found that further increase in the sintering temperature did not cause the expected density increase, but led to the gradual melting of ceramics. On the base of the results obtained during the study, one can suppose that temperature of sintering of BiNbO₄ ceramics should not exceed $T = 950^\circ\text{C}$. Also, doping bismuth niobate with additives that lower the sintering temperature can lead to better density of the BiNbO₄ material, and consequently improve the basic properties. For this reason, it will be the main objective of our further research.

Acknowledgements

The present research has been supported by Polish Ministry of Education and Science from the funds for science in 2011-2014, as a research project N N507218540.

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