D. CZEKAJ[*], A. LISIŃSKA-CZEKAJ[*], K. OSIŃSKA[*], K. BIERNACKI[*]

EFFECT OF Bi_2O_3 EXCESS ON MORPHOLOGY AND STRUCTURE OF $BiNbO_4$ CERAMICS

WPŁYW NADMIARU Bi_2O_3 NA MORFOLOGIĘ I STRUKTURĘ CERAMIKI $BiNbO_4$

Goal of the present research was to fabricate $BiNbO_4$ ceramics from the mixture of powders by the solid state reaction route and pressureless sintering at various temperatures (T_S =870^{0}C and T_S =910^{0}C) and study microstructure, phase composition and crystalline structure of $BiNbO_4$ ceramics. Four batches were fabricated and examined, namely the one fabricated from the stoichiometric mixture of reagent – grade oxide powders, viz. Bi_2O_3 and Nb_2O_5 as well as the ones with an excess of 3%, 5% and 10% by mole of Bi_2O_3. It was found that apart from the main orthorhombic α-$BiNbO_4$ phase additional phases, namely tetragonal $Bi_5Nb_3O_{15}$, and cubic Bi_3NbO_7 are possible to form from the mixture of bismuth oxide and niobium oxide. It was found that α-$BiNbO_4$ ceramics exhibited the orthorhombic symmetry identified as *Pnna* (52). However, small differences in elementary cell parameters were found for the samples sintered from stoichiometric and non-stoichiometric mixture of initial powders.

Keywords: $BiNbO_4$ ceramics, pressureless sintering, X-ray diffraction, phase analysis, crystal structure

Celem niniejszej pracy było wytworzenie ceramiki $BiNbO_4$ z mieszaniny proszków metodą reakcji w fazie stałej z następującym spiekaniem swobodnym przeprowadzonym w temperaturze T_S =870^{0}C i T_S =910^{0}C. Ponadto zbadano wpływ zawartości Bi_2O_3 na mikrostrukturę, skład chemiczny, fazowy i strukturę krystaliczną ceramiki $BiNbO_4$. Mieszaniny tlenków wyjściowych Bi_2O_3 i Nb_2O_5 przygotowano zarówno w ilości stechiometrycznej, jak i z nadmiarem tlenku bizmutu odpowiednio 3%mol, 5%mol i 10%mol. Na podstawie rentgenowskiej fazowej analizy stwierdzono, że oprócz głównej fazy rombowej $\alpha-BiNbO4$ wytworzona ceramika zawiera niewielkie domieszki fazy tetragonalnej $Bi_5Nb_3O_{15}$ i regularnej Bi_3NbO_7. Stwierdzono, że faza $\alpha-BiNbO_4$ wykazuje symetrię rombową opisywaną jako *Pnna* (52), natomiast niestechiometryczność mieszaniny proszków wyjściowych powoduje niewielkie różnice parametrów komórki elementarnej

1. Introduction

Applications of microwave dielectric ceramics in the mobile communication system, such as resonators and band-pass filters duplexers, have been tremendously increasing in the last decade, due to their high reliability, high integration potential, good dielectric properties [1]. Most of the known commercial microwave dielectrics such as complex perovskite compounds: $Sn_xZr_{1-x}TiO_3$ $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$(BMT) exhibit excellent microwave dielectric properties. However, they can be sintered only at very high temperatures greater than 1400°C [1,2].

The so-called passive integration, i.e. integration of passive components such as capacitors, resistors, inductors and line resonators into the substrate carrying the integrated circuits is used for miniaturization. This passive integration is performed using multilayer ceramics technology, whereby green ceramic tapes of different materials – corresponding to the different passive functions – are laminated and co-fired usually at rather low temperatures with low loss and low melting point electrode such as Ag or Cu [1]. Therefore, it is necessary to find the microwave dielectric ceramics with low sintering temperatures and excellent microwave dielectric properties.

Bismuth-based dielectric ceramics were well known as low-fired materials and had been investigated for the application as multilayer ceramics capacitors [2]. Recently, bismuth niobate ($BiNbO_4$) has been reported to be a promising microwave dielectric ceramics due to its high quality factor (Q =14000), small temperature coefficient of resonance frequency (~50 ppm/°C), and relatively low dielectric constant (~45) [1,2,4,3].

Goal of the present research was to fabricate $BiNbO_4$ ceramics from the mixture of powders by the solid state reaction route and pressureless sintering at various temperatures and study thermal and mass effects taking place on heating the mixture of powders (by simultaneous thermal analysis), revise the morphology (SEM), crystalline structure and phase composition of sintered ceramics (by X-ray diffraction method and EDS) as well as to reveal the influence of Bi_2O_3 excess (used in the course of ceramics fabrication) on final properties of bulk ceramics.

[*] UNIVERSITY OF SILESIA, DEPARTMENT OF MATERIALS SCIENCE, 2 ŚNIEŻNA STR., 41-200 SOSNOWIEC, POLAND

2. Experimental

The samples of BiNbO$_4$ chemical composition were synthesized using the solid state reaction method. An appropriate amount of reagents – grade oxide powders, viz. Bi$_2$O$_3$ and Nb$_2$O$_5$ were thoroughly weighted in stoichiometric amount to provide conditions for formation of the desired composition, given in Eq. (1):

$$Bi_2O_3 + Nb_2O_5 \rightarrow 2BiNbO_4 \qquad (1)$$

Also three sets of experiments with non-stoichiometric mixture of bismuth oxide and niobium oxide have been performed. Namely, an excess of 3%, 5% and 10% by mole of Bi$_2$O$_3$ has been utilized. Then the mixture of oxides was ground with an agate mortar and pestle first. After that the chemicals were wet ground in polyamide bottles using zirconia balls and ethanol as a medium for 24 h to get proper mixing and surface active fine powder. The planetary ball mill was utilized for wet grinding of the powders. A small amount of ethyl alcohol and zirconia balls as grinding medium were used in the milling/homogenizing treatment that lasted for $t =24$h. After milling the powders were subjected for drying. Then the dried mixture of powders was compacted into pellets of 20 mm in diameter by pressing under pressure of $p =30$ MPa in a stainless – steel die. The green bodies were then placed in an alumina crucible and fired with air at $T =800°$C (the heating rate 5°C/min, the soaking time $t =2$h) to conduct the solid state reaction. After thermal treatment the pellets were crushed in a mortar and the synthesized material was subjected to wet milling and drying again. Phase composition of the synthesized powder was checked with X-ray diffraction method. Apart from α-BiNbO$_4$ phase a small amount of additional phases like Bi$_5$Nb$_3$O$_{15}$, Bi$_3$NbO$_7$ and Bi$_3$Nb$_{17}$O$_{47}$ was detected. Before sintering the compacts were formed in a stainless – steel die of 10 mm in diameter. Sintering was performed by pressureless sintering under ambient air in a furnace at temperature $T =870°$C and $T =910°$C and soaking time t=2h. Then the fabricated BiNbO$_4$ ceramics were characterized in terms of phase composition, microstructure and crystal structure.

Microstructure and chemical composition of the final ceramics were investigated by scanning electron microscope (SEM) HITACHI S–4700 equipped with an energy dispersive spectrometer (EDS) NORAN Vantage.

The crystal structure of ceramics was studied by X-ray diffraction method at room temperature (XPert-Pro diffractometer, $\Theta – 2\Theta$ mode, CoKα radiation, detector scan step $\Delta 2\Theta =0.01^0$ and a counting time $t =100$s). Phase analysis of X-ray diffraction patterns of BiNbO$_4$ powders was carried out using Match! (Crystal Impact) computer program [4]. As the diffraction data were raw (profile) data, the so-called "raw data processing" had to be carried out. That included: stripping of the alpha-2-radiation, data smoothing, peak searching, profile fitting, and correction for errors. The goal was to obtain a list of peaks (2Θ and intensity values) with highest possible precision. It is extremely important that this step is performed as accurate as possible in order to obtain reasonable results in the search-match process later on.

The structural analysis was performed with X'pert High-Score Plus software (PANalytical B.V). The latest available ICSD [7], ICDD [7] and IUCr/COD/AMCSD [7], databases were utilized. Refinement of the structural parameters of BiNbO$_4$ ceramics was performed with the Rietveld method [e.g.7].

3. Results and discussion

3.1. Thermal behavior of the powders

Simultaneous thermal analysis (STA), in which both thermal analysis (DTA) and mass change effects (TG) are measured concurrently on the same sample was used to investigate synthesis effects in the stoichiometric mixture of powders (viz. Bi$_2$O$_3$ and Nb$_2$O$_5$). The measurements were obtained with Netzsch STA409 thermal analyzer and results of STA of the oxides forming BiNbO$_4$ compound are given by us elsewhere [5, 6]. Let us only mention that the main mass change effects took place within the temperature range $T =200°$C – 500°C. At temperature $T =500°$C the total mass change was $\Delta m =$-0.78%. Further increase in temperature was not accompanied with any mass change effects. DTA analysis revealed an existence of an exothermic peak at $T \approx 860°$C (formation of α-BiNbO$_4$, i.e. orthorhombic form of bismuth niobate) [11] as well as two endothermic peaks that appeared at $T \approx 1067°$C and $T \approx 1186°$C [12]. Taking into consideration published phase diagrams of Bi$_2$O$_3$-Nb$_2$O$_5$ system [e.g. 7 and references cited therein] one can conclude that the first peak corresponds to decomposition of the possible minor phase Bi$_5$Nb$_3$O$_{15}$ into Bi$_3$NbO$_7$ and transformation of low temperature α-BiNbO$_4$ into high temperature β-BiNbO$_4$ phase. It is worth noting that structural phase transition from α- to β-BiNbO$_4$ takes place at $T \approx 1020°$C whereas, Bi$_5$Nb$_3$O$_{15}$ is unstable at $T =1050°$C [13]. At temperature $T>1020°$C Bi$_3$NbO$_7$ is likely to exist as a minor phase together with β-BiNbO$_4$. Above $T>1110°$C only high temperature BiNbO$_4$ phase is possible to exist in bismuth-rich Bi$_2$O$_3$-Nb$_2$O$_5$ system [13]. Therefore, one can suppose that the second above-mentioned endothermic peak at $T \approx 1186°$C corresponds to decomposition of Bi$_3$NbO$_7$ and melting of β-BiNbO$_4$ phase.

3.2. Morphology and chemical composition of ceramics

SEM pictures of BiNbO$_4$ ceramics obtained by pressureless sintering from stoichiometric and non-stoichiometric mixtures of oxides are shown in Fig. 1.

One can see from Fig. 1 that neither an excess of Bi$_2$O$_3$ (Fig. 1a, c or Fig. 1b, d) nor an increase in temperature (Fig. 1a, b or Fig. 1c, d) change the morphology of ceramics in a substantial way. Grains of about 1μm in diameter constitute relatively porous ceramics. Application of an excess of Bi$_2$O$_3$ does not improve porosity of ceramic samples under study.

Results of the calculations performed on the basis of the EDS measurements spectra for BiNbO$_4$ ceramics sintered at Ts=870°C and Ts=910°C from both stoichiometric mixture of oxides and from mixtures including an excess of Bi$_2$O$_3$ are shown in Fig. 2. One can see from Fig. 2 that an increase in the sintering temperature from Ts=870°C to Ts=910°C does not influence significantly the chemical composition of ceramics. On the other hand, all traces shown in Fig. 2 exhibit 'sigmoidal' shape in relation to Bi$_2$O$_3$ excess in the initial

mixture. This can be explained in terms of thermal behavior of Bi_2O_3 [8]. The higher is an amount of Bi_2O_3 excess in the initial mixture of oxides the smaller is the deviation from the. stoichiometric $BiNbO_4$ composition (dashes straight lines in Fig. 2) after sintering. One can estimate from Fig. 2 that for achieving the stoichiometric composition of $BiNbO_4$ ceramics subjected to pressureless sintering in ambient air at $T_S = 910°C$ an excess of 10 mol% of Bi_2O_3 oxide is necessary while if sintering is performed at $T_S = 870°C$ an excess of Bi_2O_3 of about 9 mol% is required.
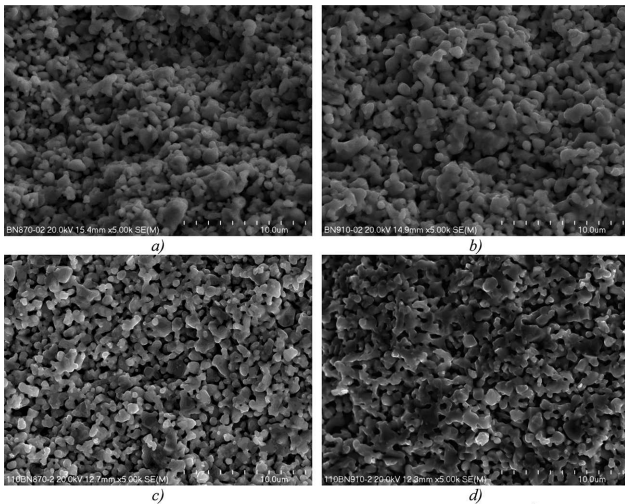
Fig. 1. Morphology of $BiNbO_4$ ceramics sintered at $Ts=8700C$ (a,c) and $Ts=9100C$ (b,d) from stoichiometric mixture of oxides (a,b) and with 10mol% excess of Bi_2O_3 (c, d)

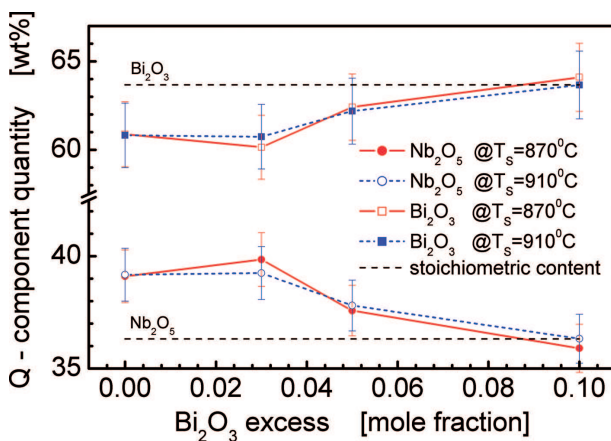Fig. 2. Composition of $BiNbO_4$ ceramics sintered at temperature $TS=8700C$ and $TS=9100C$ expressed in the mole fraction of constituting oxides, viz. Bi_2O_3 and Nb_2O_5

3.3. Crystal structure

As an example, X-ray diffraction patterns of $BiNbO_4$ ceramics sintered at $T_S = 870°C$ and $T_S = 910°C$ from stoichiometric mixture of Bi_2O_3 and Nb_2O_5 oxides as well as from a mixture with an excess amount of 10 mol% of Bi_2O_3 are shown in Fig. 3 (raw data). Also diffraction lines of the possible phases ($BiNbO_4$ and $BiNb_3O_{15}$) are shown. One can see from Fig. 3 that diffraction peaks present in the pattern could

matched the appropriate phase. The search-match procedure was performed after raw data processing.

Fig. 3. Comparison of X-ray diffraction patterns of $BiNbO_4$ ceramics with diffraction lines positions of major (α-$BiNbO_4$) and minor ($Bi_5Nb_3O_{15}$) phases

Phase analysis of X-ray diffraction patterns has shown that $BiNbO_4$ ceramics fabricated during the present study was multiphase and apart from the major phase of bismutocolumbite $BiNbO_4$ (PDF card No 01-082-0348; total number of peaks 124; 109 peaks in the range, matched 93 peaks; Figure-of-Merit, i.e. a number which is calculated from the various measures of agreement between database and unknown pattern, $FoM = 0.871$) a small amount of minor phases like $Bi_5Nb_3O_{15}$ (PDF card No 00-039-0939; total number of peaks 8; 8 peaks in the range; matched 8 peaks; $FoM = 0694$) and Bi_3NbO_7 (PDF card No 01-086-0875; total number of peaks 9; 8 peaks in the range; matched 8 peaks; $FoM = 0.737$). Unfortunately, only qualitative phase analysis was possible due to fact that crystallographic information files mentioned above did not contain enough data necessary to perform semi-quantitative analysis using the "Reference Intensity Ratio method"[9].

Detailed structural analysis of X-ray diffraction patterns was performed with Rietveld method. A model structure of α-$BiNbO_4$ (orthorhombic symmetry, $Pnna$(52) space group) according to the ICSD database (code 97422) was taken as an initial structure for structural parameters refinement. Results of the calculations are shown in Fig. 4-Fig. 6. It was found that the elementary cell parameters change slightly in the following range: $a = 5.679$-5.680Å, $b = 11.710$-11.712Å and $c = 4.982$-4.983Å.

Dependence of the calculated elementary cell volume on an excess amount of Bi_2O_3 (Fig. 4) show that after initial increase, the volume decreases with an increase in Bi_2O_3. Taking into consideration that the ionic radius of $Bi^{3+} = 1.2$Å is almost two times larger that the ionic radius of $Nb^{5+} = 0.7$Å an increase in bismuth amount in $BiNbO_4$ compound (Fig. 2) can stand for an increase in the elementary cell volume. Further decrease in α-$BiNbO_4$ elementary cell may be due to increase in an amount of $Bi_5Nb_3O_{15}$ impurity phase which can cause deficiency in bismuth ions in $BiNbO_4$ compounds. This can be seen in Fig. 3 as an increase in intensity of the diffraction line at the angle $2\theta = 14.75^0$-14.80^0. However, more detailed measurements (and/or calculations) should be performed to justify the above mentioned hypothesis.
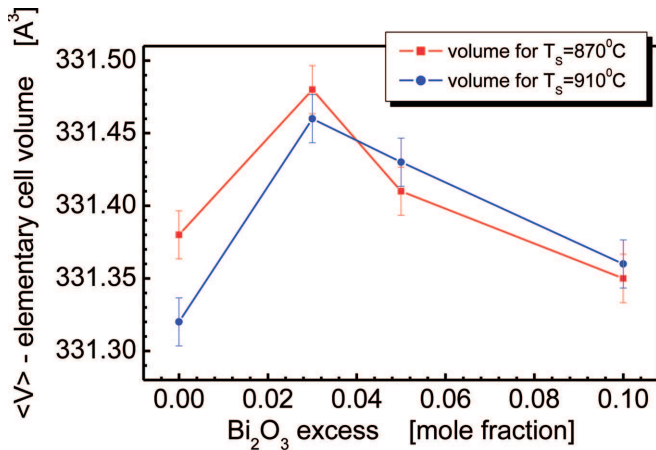
Fig. 4. Dependence of the elementary cell volume on excess amount of Bi_2O_3 oxide

Effect of sintering temperature on the elementary cell volume also changes with an increase in Bi_2O_3 amount. One can estimate from Fig. 4 that for an excess amount of Bi_2O_3 less than c.a. 4 mol% higher sintering temperature causes the smaller elementary cell volume of α-BiNbO$_4$ compound whereas for Bi_2O_3 excess amount >4 mol% higher sintering temperature leads to an increase in the elementary cell volume.

Dependence of the average crystallite size of α-BiNbO$_4$ compound on an excess amount of Bi_2O_3 at different sintering temperatures is shown in Fig. 5. Higher sintering temperature causes larger mean dimensions of crystallites (expected phenomenon). One can also see in Fig. 5 that the higher is an amount of Bi_2O_3 in the mixture of initial oxides the smaller is the difference in mean dimensions of crystallites caused by the sintering temperature and both curve runs tend to achieve a value of c.a $<D> \approx 900$Å.
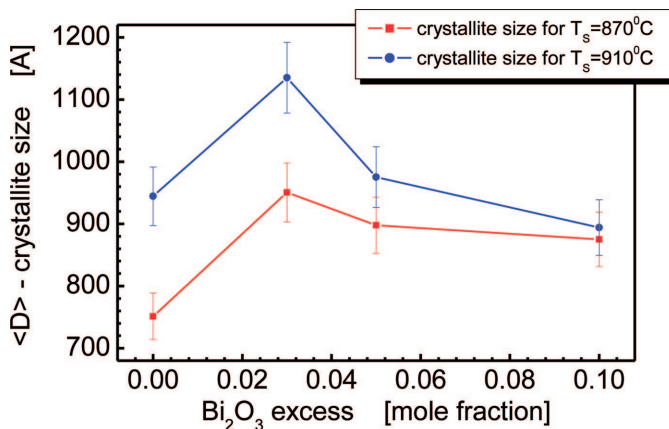

Fig. 5. Dependence of the average crystallite size on excess amount of Bi_2O_3 oxide

Dependence of the average micro strain on excess amount of Bi_2O_3 shown in Fig. 6 proves quality of the crystalline structure of fabricated α-BiNbO$_4$ compound. One can see in Fig. 6 that in case of lower sintering temperature (i.e. $T_S = 870°C$) micro deformations calculated for orthorhombic structure of α-BiNbO$_4$ compound decrease with a local minimum (i.e. non-monotone) at 3mol% of Bi_2O_3. On the other hand, ceramic samples sintered at higher temperature, (i.e. $T_S = 910°C$) exhibited an increase of the average micro strain with an in-

crease in an excess amount of Bi_2O_3. Both curve runs tend to achieve value of c.a. $<\Delta d/d> \approx 0.04\%$.
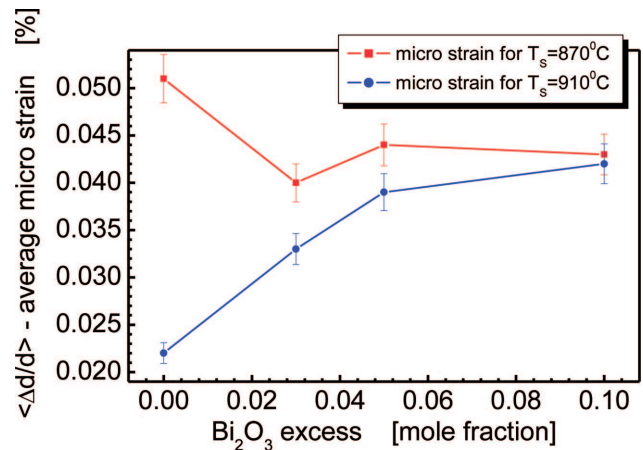

Fig. 6. Dependence of the average strain on excess amount of Bi_2O_3 oxide

4. Conclusions

By means of the mixed oxide method followed by pressureless sintering BiNbO$_4$ ceramics was successfully fabricated from both stoichiometric and non-stoichiometric mixture of Bi_2O_3 and Nb_2O_5 powders, via the solid state reaction route. It was found that BiNbO$_4$ ceramics sintered in ambient air exhibited multiphase composition i.e. apart from the major α-BiNbO$_4$ phase the tetragonal $Bi_5Nb_3O_{15}$ and cubic Bi_3NbO_7 phases were present. The chemical composition of the sintered ceramics changes with composition of the initial mixture of powders. It was revealed that an excess of 10 mol% or 9 mol% of Bi_2O_3 is necessary for achieving the theoretical composition of BiNbO$_4$ when sintering is performed at $T_S = 910°C$ or $T_S = 870°C$, respectively. However, an excess of Bi_2O_3 in amount of 3-10mol% did not improve density of ceramics.

It was found that BiNbO$_4$ ceramics, adopted the orthorhombic crystal structure described as *Pnna* (SG 52) (α-BiNbO$_4$) with the elementary cell parameters differing in $\pm 0.02\%$, namely: $a = 5.679$-5.680Å, $b = 11.710$-11.712Å and $c = 4.982$-4.983Å. Average crystallite size of α-BiNbO$_4$ changed within the range $<D> = 751$-951Å and $<D> = 894$-1135Å at $T_S = 870°C$ and $T_S = 910°C$, respectively, whereas microdeformations $<\Delta d/d> = 0.04$-0.051% and $<\Delta d/d> = 0.022$-0.042% for samples sintered at $T_S = 870°C$ and $T_S = 910°C$, respectively.

Acknowledgements

REFERENCES

[1] W. W e r s i n g, Microwave ceramics for resonators and filters, Current Opinion in Solid State and Materials Science **1**, 5, 715-731 (1996).

[2] N. W a n g, M.-Y. Z h a o, Z.-W. Y i n, W. L i, Effects of complex substitution of La and Nd for Bi on the microwave dielectric properties of BiNbO$_4$ ceramics, Materials Research Bulletin **39**, 439-448 (2004).

[3] H. K a g a t a, T. I n o u e, J. K a t o, I. K a m e y a m a, Low-fire bismuth-based dielectric ceramics for microwave use, Jpn. J. Appl. Phys. **31**, 3152 (1992).

[4] MATCH! Version 2.0.11, CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany (URL: http://www.crystalimpact.com/match).

[5] A. L i s i ń s k a - C z e k a j, D. C z e k a j, Fabrication and study of BiNbO$_4$ ceramics, Key Engineering Materials **512-515**, 1212-1217 (2012).

[6] M. P ł o ń s k a, D. C z e k a j, Studies of temperature and fabrication methods influence on structure and microstructure of BiNbO$_4$ microwave electroceramics, Archives of Metallurgy and Materials **56**, 4, 1169-1175 (2011).

[7] Ch.D. L i n g, R.L. W i t h e r s, S. S c h n i d t, J.G. T h o m - s o n, A review of bismuth-rich binary oxides in the systems Bi$_2$O$_3$-Nb$_2$O$_5$, Bi$_2$O$_3$-Ta$_2$O$_5$, Bi$_2$O$_3$-MoO$_3$, and Bi$_2$O$_3$-WO$_3$, Journal of Solid State Chemistry **137**, 42-61 (1998).

[8] A. L i s i ń s k a - C z e k a j, D. C z e k a j, Synthesis of Bi$_5$TiNbWO$_{15}$ ceramics, Archives of Metallurgy and Materials **54**, 4, 869-874 (2009).

[9] I.S. Y a k i m o v, P.S. D u b i n i n, O.E. P i k s i n a, Method of regularized multipeak reference intensity ratio for quantitative X-ray phase analysis of polycrystalline materials, Inorganic Materials **47**, 15, 1681-1686 (2011).