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EFFECTS OF V₂O₅ ADDITIVE ON STRUCTURE AND DIELECTRIC PROPERTIES OF BiNbO₄ CERAMICS

WPLYW V₂O₅ NA STRUKTURĘ I WŁAŚCIWOŚCI DIELEKTRYCZNE CERAMIKI BiNbO₄

Goal of the present research was to investigate the influence of V₂O₅ additive on the structure and dielectric properties of BiNbO₄ ceramics. To fabricate BiNbO₄ ceramics with V₂O₅ added the solid state reaction route and pressureless sintering was utilized. Thus obtained ceramics was characterized in terms of its microstructure (SEM), chemical composition (EDS), phase composition and crystalline structure (X-ray phase and structural analysis, respectively). Also dielectric properties in both temperature and frequency domains were investigated. The impedance spectroscopy was utilized for dielectric characterization and the measurements of complex impedance were performed within the frequency range $\nu = 10\text{Hz} - 1\text{MHz}$ and temperature range $T = \text{RT} - 550^\circ\text{C}$. It was found that V₂O₅ additive changed slightly lattice parameters of BiNbO₄ ceramics, decreased porosity of samples and revealed relaxation phenomena within the frequency ranges $\nu = 10^2 - 10^3\text{ Hz}$ and $\nu = 10^5 - 10^6\text{ Hz}$ at temperature $T > 285^\circ\text{C}$.

Keywords: BiNbO₄ ceramics, V₂O₅ additive, morphology, crystal structure, phase analysis, dielectric properties

Celem niniejszej pracy było zbadanie wpływu dodatku V₂O₅ na strukturę i właściwości dielektryczne ceramiki BiNbO₄. Do wytworzenia ceramiki zastosowano metodę reakcji w fazie stałej i spiekanie swobodne w atmosferze powietrza. Ceramikę poddano badaniom morfologii (SEM), składu chemicznego (EDS) oraz rentgenowskiej analizie fazowej i strukturalnej. Właściwości dielektryczne w domenie częstotliwości ($\nu = 10\text{Hz} - 1\text{MHz}$) i temperatury ($T = \text{RT} - 550^\circ\text{C}$) zbadano przy pomocy spektroskopii impedancyjnej. Stwierdzono, że dodatek V₂O₅ powoduje niewielką zmianę parametrów komórki elementarnej, zmniejsza porowatość ceramiki oraz pozwolił zaobserwować zjawiska relaksacyjne występujące w dwóch zakresach częstotliwości: $\nu = 10^2 - 10^3\text{ Hz}$ oraz $\nu = 10^5 - 10^6\text{ Hz}$ w temperaturze $T > 285^\circ\text{C}$.

1. Introduction

To apply the multilayer technology, development of a dielectric material suitable for co-firing with internal conductors below the melting temperature of the metals has become a major focus. The search for high-dielectric constant materials with high temperature stability and a low dissipation factor was initiated. The development began with the search for a suitable low-firing-temperature dielectric, and then the modification of the electrical characteristics to meet the above requirements for the resonators and filters [1, 2].

Bismuth niobate (BiNbO₄) has been reported to be a promising microwave dielectric ceramics [3] and now BiNbO₄ ceramics exhibiting an α -phase [4, 5, 6] are worldwide investigated microwave materials [7, 8, 9]. However, various attempts have been undertaken to improve the microwave dielectric properties of BiNbO₄, such as the substitution of lanthanide for Bi [10], the solid solutions of Bi(Nb_{1-x}Ta_x)O₄, Bi(Nb_{1-x}Sb_x)O₄ and the addition of various sintering aids [11]. However, the effect of the additives on low frequency dielectric characteristics of BiNbO₄ ceramics was not reported. It is interesting to clarify the relationship above.

In this paper BiNbO₄ ceramics were chosen as a host material to be sintered with a sintering aid V₂O₅. It is commonly known [1, 3] that sinterability of BiNbO₄ ceramics with less than 0.125wt%V₂O₅ added was not improved well even when the sintering temperature was at $T = 955^\circ\text{C}$. Therefore in our research concentration of V₂O₅ additive was taken as within the range: $c_W = 0.125 - 2.0\text{ wt\%}$. The sintering behavior and low frequency dielectric characteristics of BiNbO₄ ceramics with different amount of additives were investigated. The resultant dielectric properties were analyzed based on the amount of V₂O₅ additive.

2. Experimental

Specimen powders were prepared by a conventional solid-state reaction technique. The mixture of reagent-grade oxide powders, viz. Bi₂O₃ and Nb₂O₅ (mixed oxide method) was prepared and subjected to pressureless (i.e. free) sintering at $T = 870^0 - 910^\circ\text{C}$, soaking time $t = 2$ hours at ambient atmosphere. Details of the preparation method as well as results of simultaneous thermal analysis (STA) of the powders, phase composition and crystal structure of sintered ceramics

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have been reported by us elsewhere [e.g. 5, 6, 12]. It is worth noting, however, that after synthesis at $T = 800^\circ\text{C}$ from stoichiometric mixture of oxides the V_2O_5 sintering additive was utilized in amount of $c_W = 0.125 - 2.0 \text{ wt}\%$.

Thus fabricated BiNbO_4 ceramics were characterized in terms of its microstructure, chemical and phase composition as well as the crystal structure. Scanning electron microscopy (HITACHI S-4700 with NORAN Vantage EDS spectrometer) as well as X-ray diffraction method at room temperature (XPert-Pro diffractometer, $\Theta - 2\Theta$ mode, $\text{CoK}\alpha/\text{CuK}\alpha$ radiation, detector scan step $\Delta 2\Theta = 0.01^\circ$ and a counting time $t=100\text{s}$) were utilized.

Dielectric properties were studied by impedance spectroscopy within the frequency range $\nu = 10\text{Hz} - 1\text{MHz}$ and temperature range $T = \text{RT} - 550^\circ\text{C}$. Precision LCR meter of Agilent E4980A – type was utilized.

3. Results and discussions

Morphology of BiNbO_4 ceramics sintered at $T_S = 910^\circ\text{C}$ with V_2O_5 additive in amount of 0.125wt% and 2wt% are shown in Fig. 1 a) and b), respectively. One can see in from Fig. 1 that V_2O_5 additive substantially influences morphology of ceramic fractures. Although the average grain size did not increase, application of V_2O_5 as a sintering aid greatly improved decrease in porosity of ceramic samples under study.

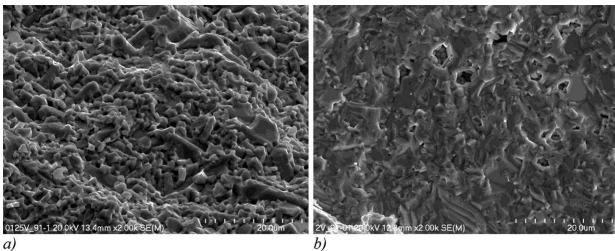


Fig. 1. Morphology of BiNbO_4 ceramics sintered at $T_S = 910^\circ\text{C}$ with V_2O_5 additive in amount of 0.125wt% (a,) and 2wt% (b)

Results of the EDS measurements are shown in Tab. 1. It is worth noting that theoretical stoichiometric composition of BiNbO_4 compound recalculated into constituting oxides is 63.68wt% of Bi_2O_3 and 36.32wt% of Nb_2O_5 . Calculations

performed on the base of the EDS measurements showed that the chemical composition of the compounds in relation to bismuth oxide and niobium oxide manifested a tendency of lack of Bi_2O_3 component (excess of Nb_2O_5). It is worth noting that in case of 2.0wt% of additive, vanadium was detected by the measuring technique.

Comparison of X-ray diffraction patterns for BiNbO_4 ceramics sintered at $T = 870^\circ\text{C}$ without and with small amount of the sintering aid is given in Fig. 2, whereas an example of X-ray diffraction structural analysis results is given in Fig. 3. One can see from Fig. 2 that X-ray diffraction patterns are almost identical and thus it may be supposed that the powders under study exhibited the same crystal structure. To justify the above statement structural analysis was performed with the help of Rietveld refinement method [13]. As an initial model structure the crystallographic information file from ICSD database was taken (ICSD database code 97422 – bismuth niobate(V); orthorhombic symmetry; $Pnna$ (52) space group). Results of the lattice parameters calculations are given in Tab. 2 and X-ray diffraction profile of the refined structure together with experimental pattern are given in Fig. 3.

One can see from Fig. 3 that there are additional diffraction lines of very small intensity (square-scale intensity axis in Fig. 3) at angle $2\theta = 25.528^\circ; 29.662^\circ; 34.396^\circ$ which can be attributed to $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ impurity phase. Unfortunately, more detailed calculations based on reference intensity ratio method [14] are not reliable due to the doubtful quality of database entry describing $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ (PDF code 00-016-0293).

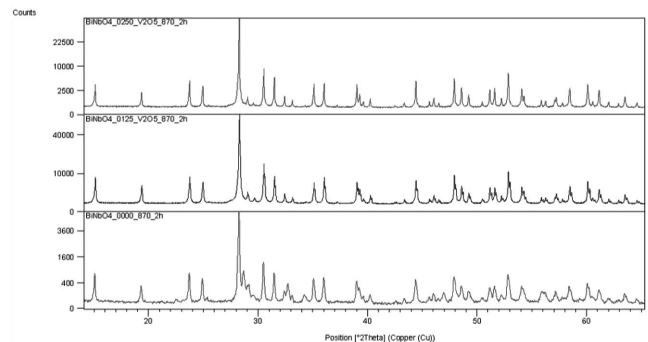


Fig. 2. Comparison of X-ray diffraction patterns of BiNbO_4 powder sintered at $T_S = 870^\circ\text{C}$

TABLE 1

Quantitative results for BiNbO_4 with 0.125wt% and 2.0wt% of V_2O_5 Correction Method: Proza (Phi-Rho-Z)

Element Line	Net counts 0.125 wt%	Net counts 2.0 wt%	Weight % 0.125 wt%	Weight% 2.0 wt%	Formula	Compound 0.125 wt%	Compound 2.0 wt%
OK	675	546	18.01S	18.55S			
VK	0	472	0.00	0.51	V_2O_5	0.00	0.91
Nb L	50497	33287	27.24	28.06	Nb_2O_5	38.97	40.14
Bi M	74774	45914	54.75	52.88	Bi_2O_3	61.03	58.95
Total			100.00	100.00		100.00	100.00

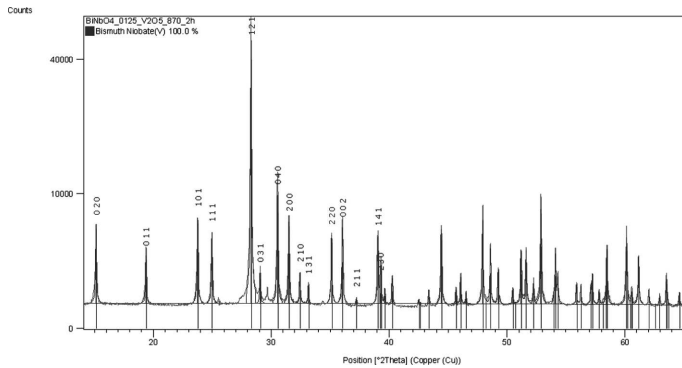


Fig. 3. X-ray diffraction structural analysis for BiNbO₄ ceramics sintered with 0.125wt% V₂O₅ additive. Miller indices are given for 15 first diffraction lines

One can see from Tab. 2 that small differences in crystallographic parameters were found. With an increase in amount of the sintering additive *a* and *c* elementary cell parameters increased, whereas *b* parameter reached maximum for 0.125wt% of V₂O₅. However, the elementary cell volume increased with an increase in amount of the additive and thus the density calculated from the X-ray diffraction patterns decreased.

TABLE 2

Lattice parameters of BiNbO₄ with 0.125wt% and 2.0wt% of V₂O₅

V ₂ O ₅ amount wt%	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	<i>V</i> [pm ³]	Density (calculated) g/cm ³
0.000	5.6791(4)	11.7109(8)	4.9822(3)	331.35190	7.3333
0.125	5.68089(7)	11.7116(1)	4.98290(6)	331.52380	7.3295
0.250	5.68116(6)	11.7111(1)	4.98302(6)	331.53230	7.3293

Dielectric behavior of BiNbO₄ ceramics both sintered from stoichiometric mixture of oxides as well as with V₂O₅ additive were studied in the frequency domain ($\nu = 10\text{Hz} - 1\text{MHz}$) at temperature stabilized within the range $T = \text{RT} - 550^\circ\text{C}$ by impedance spectroscopy. The Kramers-Kronig data validation test [15, 16] was employed in the impedance data analysis according to the strategy reported by us elsewhere [e.g. 17, 18]. It is worth noting, that ceramic samples subjected to electrical measurements were of 1 mm thick and 10 mm in diameter. Surface of the samples was polished and round-shaped electrodes were deposited on both sides of the disk-shaped ceramics (silver paste was used).

Results of dielectric permittivity measurements are given in Fig. 4 and Fig. 5. One can see from Fig. 4 that for non-modified BiNbO₄ ceramics the real part of dielectric permittivity exhibited rather smooth (in a log-log scale) dependence on frequency. On the other hand, V₂O₅ additive caused appearance of irregularities in form of “shoulders” revealed either by temperature (Fig. 4b) or frequency (Fig. 4c). Also the additive caused an increase in dielectric permittivity value at frequency close to the end of the measuring range.

The dependence of imaginary part of dielectric permittivity on frequency showed in Fig. 5 differs substantially for different amount of V₂O₅ additive. One can see that maxima on Fig. 5c appeared at frequency $\nu = 10^5 - 10^6\text{Hz}$ which shifted toward higher frequency with an increase in temperature. But only spectroscopic plots of dielectric loss tangent

(which is a ratio of the real and imaginary part of dielectric permittivity) revealed possible relaxation phenomena at lower frequency range for V₂O₅-modified BiNbO₄ ceramics (Fig. 6b and c). For ceramics with 0.125wt% V₂O₅ additive the maxima appeared at $\nu = 10^2 - 10^3\text{Hz}$ at temperature starting from $T = 285^\circ\text{C}$ (Fig. 6b) whereas for 2.0wt% V₂O₅ additive they manifested themselves starting from $T = 423^\circ\text{C}$ in a form of “shoulders” first.

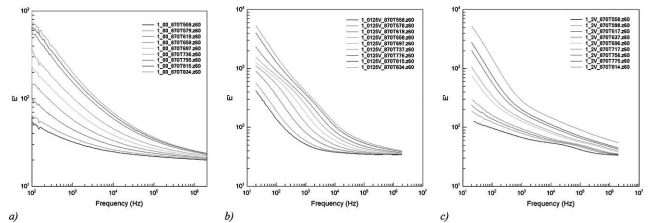


Fig. 4. Spectroscopic plots of real part of dielectric permittivity for pure (a) and V₂O₅-modified BiNbO₄ ceramics: 0.125wt% (b) and 2.0wt% (c)

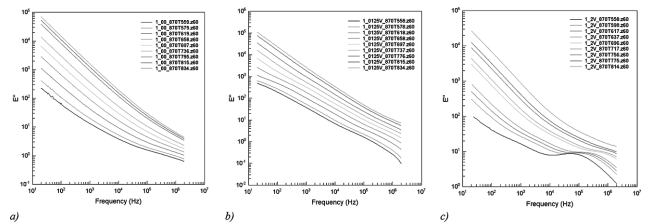


Fig. 5. Spectroscopic plots of imaginary part of dielectric permittivity for pure (a) and V₂O₅-modified BiNbO₄ ceramics: 0.125wt% (b) and 2.0wt% (c)

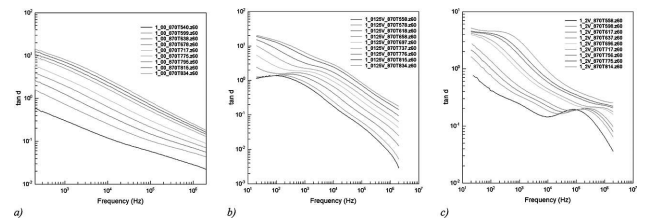


Fig. 6. Spectroscopic plots of dielectric loss tangent for pure (a) and V₂O₅-modified BiNbO₄ ceramics: 0.125wt% (b) and 2.0wt% (c)

4. Conclusion

In the present study BiNbO₄ ceramics with V₂O₅ sintering aid was fabricated by pressureless sintering in ambient air. It was found that V₂O₅ additive had an effect on morphology of ceramic fractures that manifested in a decrease of porosity of ceramic samples. Chemical composition of the compounds estimated by EDS technique showed a tendency of lack of Bi₂O₃ component. It was found that BiNbO₄ ceramics adopted the orthorhombic symmetry described with *Pnma* (52) space group. However, small differences in crystallographic parameters were found. The elementary cell volume increased with an increase in amount of the additive and thus the density calculated from the X-ray diffraction patterns decreased. Impedance spectroscopy showed that the additive of V₂O₅ caused an increase in the modulus of dielectric permittivity. However, the dielectric losses were found to decrease

by adding the additive. Dielectric relaxation peaks one could observe on spectroscopic plots of dielectric loss tangent that shifted toward high frequency with an increase in temperature.

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REFERENCES

- [1] Ch.-L. H u a n g, M.-H. W e n g, G.-M. S h a n, Effect of V_2O_5 and CuO additives on sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics, *Journal of Materials Science* **35**, 5443-5447 (2000).
- [2] W. W e r s i n g, Microwave ceramics for resonators and filters, *Current Opinion in Solid State and Materials Science* **1**, 715-731 (1996).
- [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] 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**, 1169-1175 (2011).
- [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] D. C z e k a j, A. L i s i Ń s k a - C z e k a j, M. A d a m c z y k, L. K o z i e l s k i, Low temperature fabrication and study of bismuth-based microwave ceramics of ABO_4 – type structure, *Proceedings of 20th Annual International Conference on Composites or Nano Engineering ICCE-20*, Beijing, China, 2012.
- [7] R. R a d h a, H. M u t h u r a j a n, N.R. K o t e s w a r a, S i v a r a m P r a d h a n, U.N. G u p t a, Low temperature synthesis and characterization of $BiNbO_4$ powders, *Materials Characterization* **59**, 1083-1087 (2008).
- [8] Y.-Ch. L i o u, W.-Ch. T s a i, H.-M. C h e n, Low-temperature synthesis of $BiNbO_4$ ceramics using reaction-sintering process, *Ceramics International* **35**, 2119-2122 (2009).
- [9] S a n g K i K o, K y u n g Y o n g K i m, B y o n g H o K i m, Characteristics of tapped microstrip bandpass filter in $BiNbO_4$ ceramics, *Journal of Materials Science: Materials in Electronics* **9**, 351-356 (1998).
- [10] 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 (2004).
- [11] E.S. K i m, W. C h o i, Effect of phase transition on the microwave dielectric properties of $BiNbO_4$, *Journal of the European Ceramic Society* **26**, 1761-1766 (2006).
- [12] D. C z e k a j, A. L i s i Ń s k a - C z e k a j, K. O s i Ń s k a, Effect of Bi_2O_3 excess on morphology and structure of $BiNbO_4$ ceramics, submitted to *Archives of Metallurgy and Materials*, 2013.
- [13] H.M. R i e t v e l d, The Rietveld method – a historical perspective, *Austr. J.Phys.* **41**, 113-116 (1988).
- [14] C.R. H u b b a r d, E.H. E v a n s, D.K. S m i t h, The reference intensity ratio for computer simulated powder patterns, *J. Appl. Crystallogr.* **169**, 169-174 (1976).
- [15] B.A. B o u k a m p, Electrochemical impedance spectroscopy in solid state ionics: recent advances, *Solid State Ionics* **169**, 65-73 (2004).
- [16] B.A. B o u k a m p, A linear Kronig-Kramers transform test for admittance data validation, *J. Electrochem. Soc.* **142**, 1885-1894 (1995).
- [17] D. C z e k a j, A. L i s i Ń s k a - C z e k a j, T. O r k i s z, J. O r k i s z, G. S m a l a r z, Impedance spectroscopic studies of sol-gel derived barium strontium titanate thin films: *J. Europ. Ceram. Soc.* **30**, 465 (2010).
- [18] A. L i s i Ń s k a - C z e k a j, Wielofunkcyjne materiały na podstawie tytanian bizmutu, Uniwersytet Śląski, Wydawnictwo Gnome, Katowice, 2012.