

A. LISIŃSKA-CZEKAJ\*, D. CZEKAJ\*, K. OSIŃSKA\*, M. ADAMCZYK\*

## EFFECTS OF $V_2O_5$ ADDITIVE ON STRUCTURE AND DIELECTRIC PROPERTIES OF $BiNbO_4$ CERAMICS

### WPLYW $V_2O_5$ NA STRUKTURĘ I WŁAŚCIWOŚCI DIELEKTRYCZNE CERAMIKI $BiNbO_4$

Goal of the present research was to investigate the influence of  $V_2O_5$  additive on the structure and dielectric properties of  $BiNbO_4$  ceramics. To fabricate  $BiNbO_4$  ceramics with  $V_2O_5$  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  $V_2O_5$  additive changed slightly lattice parameters of  $BiNbO_4$  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:**  $BiNbO_4$  ceramics,  $V_2O_5$  additive, morphology, crystal structure, phase analysis, dielectric properties

Celem niniejszej pracy było zbadanie wpływu dodatku  $V_2O_5$  na strukturę i właściwości dielektryczne ceramiki  $BiNbO_4$ . 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 zakresie 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  $V_2O_5$  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 ( $BiNbO_4$ ) has been reported to be a promising microwave dielectric ceramics [3] and now  $BiNbO_4$  ceramics exhibiting an  $\alpha$ -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  $BiNbO_4$ , such as the substitution of lanthanide for Bi [10], the solid solutions of  $Bi(Nb_{1-x}Ta_x)O_4$ ,  $Bi(Nb_{1-x}Sb_x)O_4$  and the addition of various sintering aids [11]. However, the effect of the additives on low frequency dielectric characteristics of  $BiNbO_4$  ceramics was not reported. It is interesting to clarify the relationship above.

In this paper  $BiNbO_4$  ceramics were chosen as a host material to be sintered with a sintering aid  $V_2O_5$ . It is commonly known [1, 3] that sinterability of  $BiNbO_4$  ceramics with less than 0.125wt%  $V_2O_5$  added was not improved well even when the sintering temperature was at  $T = 955^\circ\text{C}$ . Therefore in our research concentration of  $V_2O_5$  additive was taken as within the range:  $c_W = 0.125 - 2.0\text{ wt\%}$ . The sintering behavior and low frequency dielectric characteristics of  $BiNbO_4$  ceramics with different amount of additives were investigated. The resultant dielectric properties were analyzed based on the amount of  $V_2O_5$  additive.

## 2. Experimental

Specimen powders were prepared by a conventional solid-state reaction technique. The mixture of reagent-grade oxide powders, viz.  $Bi_2O_3$  and  $Nb_2O_5$  (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

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

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  $\text{V}_2\text{O}_5$  sintering additive was utilized in amount of  $c_W = 0.125 - 2.0 \text{ wt}\%$ .

Thus fabricated  $\text{BiNbO}_4$  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  $\text{BiNbO}_4$  ceramics sintered at  $T_s = 910^\circ\text{C}$  with  $\text{V}_2\text{O}_5$  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  $\text{V}_2\text{O}_5$  additive substantially influences morphology of ceramic fractures. Although the average grain size did not increase, application of  $\text{V}_2\text{O}_5$  as a sintering aid greatly improved decrease in porosity of ceramic samples under study.

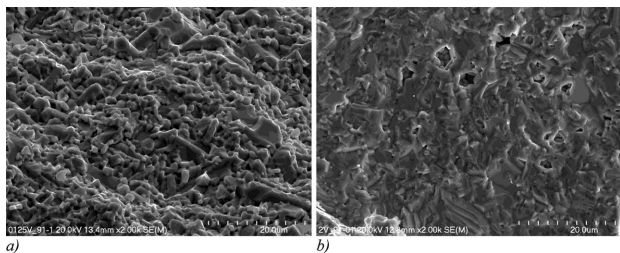


Fig. 1. Morphology of  $\text{BiNbO}_4$  ceramics sintered at  $T_s = 910^\circ\text{C}$  with  $\text{V}_2\text{O}_5$  additive in amount of 0.125wt% (a,) and 2wt% (b)

Results of the EDS measurements are shown in Tab. 1. It is worth noting that theoretical stoichiometric composition of  $\text{BiNbO}_4$  compound recalculated into constituting oxides is 63.68wt% of  $\text{Bi}_2\text{O}_3$  and 36.32wt% of  $\text{Nb}_2\text{O}_5$ . 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  $\text{Bi}_2\text{O}_3$  component (excess of  $\text{Nb}_2\text{O}_5$ ). 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  $\text{BiNbO}_4$  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).

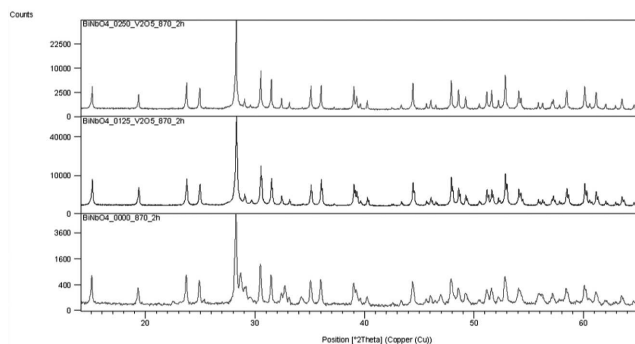


Fig. 2. Comparison of X-ray diffraction patterns of  $\text{BiNbO}_4$  powder sintered at  $T_s = 870^\circ\text{C}$

TABLE 1

Quantitative results for  $\text{BiNbO}_4$  with 0.125wt% and 2.0wt% of  $\text{V}_2\text{O}_5$  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	$\text{V}_2\text{O}_5$	0.00	0.91
Nb L	50497	33287	27.24	28.06	$\text{Nb}_2\text{O}_5$	38.97	40.14
Bi M	74774	45914	54.75	52.88	$\text{Bi}_2\text{O}_3$	61.03	58.95
Total			100.00	100.00		100.00	100.00

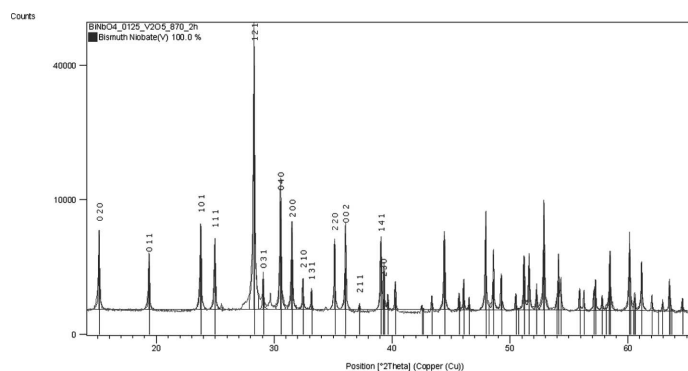


Fig. 3. X-ray diffraction structural analysis for BiNbO<sub>4</sub> ceramics sintered with 0.125wt% V<sub>2</sub>O<sub>5</sub> additive. Miller indices are given for 15 first diffraction lines

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 V<sub>2</sub>O<sub>5</sub>. 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 BiNbO<sub>4</sub> with 0.125wt% and 2.0wt% of V<sub>2</sub>O<sub>5</sub>

V <sub>2</sub> O <sub>5</sub> amount wt%	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	<i>V</i> [pm <sup>3</sup> ]	Density (calculated) g/cm <sup>3</sup>
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 BiNbO<sub>4</sub> ceramics both sintered from stoichiometric mixture of oxides as well as with V<sub>2</sub>O<sub>5</sub> 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 BiNbO<sub>4</sub> ceramics the real part of dielectric permittivity exhibited rather smooth (in a log-log scale) dependence on frequency. On the other hand, V<sub>2</sub>O<sub>5</sub> 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 V<sub>2</sub>O<sub>5</sub> 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 V<sub>2</sub>O<sub>5</sub>-modified BiNbO<sub>4</sub> ceramics (Fig. 6b and c). For ceramics with 0.125wt% V<sub>2</sub>O<sub>5</sub> 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% V<sub>2</sub>O<sub>5</sub> additive they manifested themselves starting from  $T = 423^\circ\text{C}$  in a form of “shoulders” first.

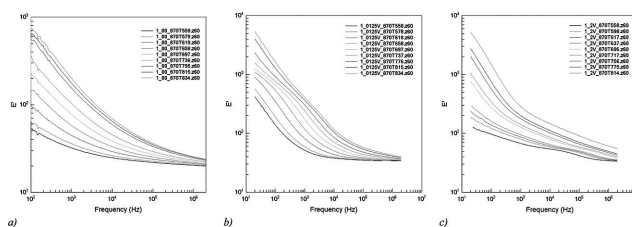


Fig. 4. Spectroscopic plots of real part of dielectric permittivity for pure (a) and V<sub>2</sub>O<sub>5</sub>-modified BiNbO<sub>4</sub> ceramics: 0.125wt% (b) and 2.0wt% (c)

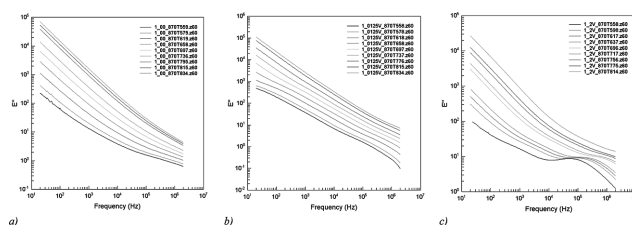


Fig. 5. Spectroscopic plots of imaginary part of dielectric permittivity for pure (a) and V<sub>2</sub>O<sub>5</sub>-modified BiNbO<sub>4</sub> ceramics: 0.125wt% (b) and 2.0wt% (c)

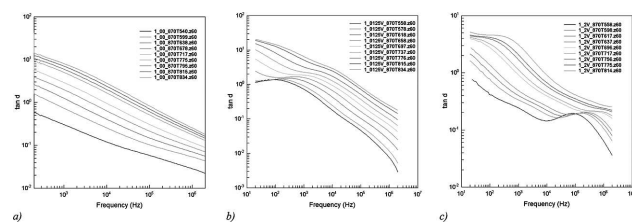


Fig. 6. Spectroscopic plots of dielectric loss tangent for pure (a) and V<sub>2</sub>O<sub>5</sub>-modified BiNbO<sub>4</sub> ceramics: 0.125wt% (b) and 2.0wt% (c)

#### 4. Conclusion

In the present study BiNbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub> sintering aid was fabricated by pressureless sintering in ambient air. It was found that V<sub>2</sub>O<sub>5</sub> 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 Bi<sub>2</sub>O<sub>3</sub> component. It was found that BiNbO<sub>4</sub> 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 V<sub>2</sub>O<sub>5</sub> 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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