A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 59 2014 Issue 1
DOI: 10.2478/amm-2014-0036

D. CZEKAJ*, A. LISIŃSKA-CZEKAJ*, M. ADAMCZYK*

INFLUENCE OF BISMUTH CONTENT ON COMPLEX IMMITTANCE CHARACTERISTICS OF PRESSURELESS SINTERED $BiNbO_4$ CERAMICS

WPŁYW ZAWARTOŚCI BIZMUTU NA ZESPOLONE CHARAKTERYSTYKI IMMITANCYJNE SPIEKANEJ SWOBODNIE CERAMIKI $BiNbO_4$

Goal of the present research was to study immittance properties of $BiNbO_4$ ceramics fabricated by the solid state reaction route followed by pressureless sintering. Four sets of samples were examined, namely the one fabricated from the stoichiometric mixture of oxides, 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. The immittance properties were studied by impedance spectroscopy. Measurements were carried out within the frequency range ν =20Hz-1MHz and temperature range T =RT-550°C. The Kramers-Kronig data validation test was employed in the impedance data analysis. It was found that complex impedance first increases with an increase in Bi_2O_3 content and decreases for 10mol% excess of Bi_2O_3. Two relaxation phenomena manifested themselves at elevated temperature (T>267°C) within the measuring frequency range. The conductivity relaxation phenomenon ($M''(\nu)$ spectra) took place at higher frequency than the phenomenon with dominant resistive component ($Z''(\nu)$ spectra).

Keywords: $BiNbO_4$ ceramics, impedance spectroscopy, impedance and modulus analysis

Celem niniejszej pracy było zbadanie właściwości immitancyjnych ceramiki $BiNbO_4$ wytworzonej metodą reakcji w fazie stałej i spiekania swobodnego. Badaniom poddano cztery zestawy próbek wytworzonych ze stechiometrycznej mieszaniny tlenków Bi_2O_3 i Nb_2O_5 oraz mieszaniny zawierającej nadmiar Bi_2O_3 w ilości 3, 5 i 10% molowych. Badania przeprowadzono z zastosowaniem spektroskopii impedancyjnej. Pomiary dokonano w zakresie częstotliwości ν =20Hz-1MHz i temperatury T =RT-550°C. Do analizy zgodności danych pomiarowych zastosowano test Kramersa-Kroniga. Stwierdzono, że ze wzrostem zawartości Bi_2O_3 w mieszaninie do 5% molowych wzrasta impedancja próbek, która dla 10% molowych maleje poniżej wartości zarejestrowanej dla $BiNbO_4$ bez nadmiaru Bi_2O_3. Zaobserwowano obecność dwóch procesów relaksacyjnych w temperaturze T>267°C. Stwierdzono, że zjawisko relaksacji przewodnictwa (widma $M''(\nu)$) zachodzi w wyższej częstotliwości niż zjawisko z dominującą składową rezystywną (widma $Z''(\nu)$).

1. Introduction

Bismuth niobate ($BiNbO_4$) has been reported to be a promising microwave dielectric ceramics [1, 2] To improve the microwave dielectric properties of $BiNbO_4$ various attempts have been undertaken. Among them one can mention e.g. addition of various sintering aids like a small amount of CuO and V_2O_5 [3, 4] both to densify the ceramics as well as to obtain higher Q value. Also substitution of lanthanide for Bi [5] or fabrication of the solid solutions of $Bi(Nb_{1-x}Ta_x)O_4$ or $Bi(Nb_{1-x}Sb_x)O_4$ is utilized [6] for dielectric properties improvement.

In our previous papers [e.g. 7, 8, 9] hot pressing method was utilized as well as an excess of small amounts of Bi_2O_3 was added to fabricate α-phase $BiNbO_4$ ceramics. However, the effect of Bi_2O_3 excess and sintering temperature on low frequency dielectric characteristics of α-phase $BiNbO_4$ was not reported. It is interesting to clarify the relationship between the structural characteristics, processing conditions and the dielectric properties to increase the application potential of low-fired microwave $BiNbO_4$ dielectric. Therefore in the present paper $BiNbO_4$ ceramics were chosen as a host material to be sintered with an excess of Bi_2O_3 at T_S =870°C. The basic dielectric properties were analyzed based on the phase composition of the $BiNbO_4$ ceramics derived from bismuth-rich Bi_2O_3-Nb_2O_5 system.

Impedance spectroscopy (IS), which is known as a powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes [10, 11] was used as a main research method. A great strength of IS is that, with appropriate data analysis, it is often possible to characterize the different electrically active regions in a material both qualitatively by demonstrating their existence and quantitatively, by measuring their individual electric properties [12]. IS may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic-ionic, and dielectrics. IS has seen a

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

tremendous increase in popularity in the recent years. Now it is a frequently used tool employed to analyze the electrical properties of a wide variety of electroceramics, including ferroelectrics, solid electrolytes and mixed conductors [13, 14, 15].

2. Experimental

$BiNbO_4$ ceramics were prepared by the conventional mixed oxide method from the mixture of oxide powders, viz. Bi_2O_3 and Nb_2O_5. However, apart from the stoichiometric composition of powders an excess of 3%, 5% and 10% by mole of Bi_2O_3 has been used to prepare green bodies. Details of the preparation method have been reported by us elsewhere [8, 9]. Also the sintered $BiNbO_4$ ceramics were characterized in terms of its phase composition as well as the crystal structure [16].

The immittance properties [10] (i.e. complex impedance, complex modulus, complex admittance, complex dielectric permittivity and dielectric losses) were studied by observing how the system responded to an electrical stimulus that was applied to the electrodes. The amplitude of the ac perturbation signal was 1V, immittance spectra were recorded automatically over the heating cycles; spectra were collected at programmed temperatures after 15 min of temperature stabilization; impedance at every frequency was measured until consistency was achieved. Precision LCR meter of Agilent E4980A – type was utilized. Measurements were carried out within the frequency range ν =20Hz-1MHz and temperature range T =RT-550°C. The Kramers-Kronig data validation test was employed in the impedance data analysis [17, 18] according to the strategy reported by us elsewhere [14, 19].

3. Results and discussions

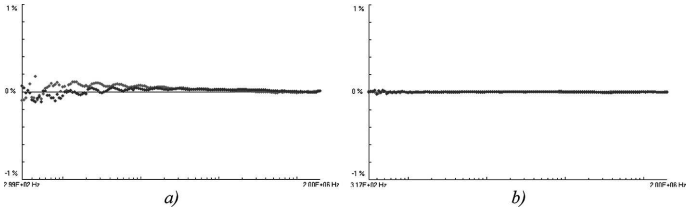
It is worth noting that ceramic samples subjected to electrical measurements exhibited orthorhombic crystal structure described as *Pnna*(52) space group (α-$BiNbO_4$ compound) with the lattice parameters differing slightly (±0.02%) with Bi_2O_3 excess. It was also found that $BiNbO_4$ ceramics fabricated from bismuth-rich Bi_2O_3-Nb_2O_5 system exhibited the multiphase composition, i.e. apart from major α-$BiNbO_4$ phase a small amount of additional phases like $Bi_5Nb_3O_{15}$, and Bi_3NbO_7 was detected [16]. Therefore, to correlate the results of the dielectric measurements with the actual phase composition of fabricated $BiNbO_4$ ceramics the assumption was made that ceramics under study consists of two phases, namely orthorhombic α-$BiNbO_4$ phase and tetragonal $Bi_5Nb_3O_{15}$ phase, what in turn is consistent with the published phase diagrams of Bi_2O_3-Nb_2O_5 system [e.g. 20].

The calculations were performed with Match! (Crystal Impact) computer program [21]. According to the methodology, the amount is calculated based on corresponding intensity scale factors (I/I_C) of the selected phases. However, in the present case the crystallographic information files describing $Bi_5Nb_3O_{15}$ (i.e. PDF cards No 00-039-0939; 00-016-0293 and 00-051-1752) did not contain the parameter I/I_C required for semi-quantitative phase analysis. Therefore, the default value I/I_C =1 was used for calculations. The above-mentioned assumption overestimated the weight percentage of the minor phase, however since all calculations were performed according to the same algorithm and the same model structures (major phase: PDF 160295; minor phase: PDF 390939) the main tendency in quantitative amount of the phases should have reflected the real situation.

As a result of calculations the following phase composition of the resultant ceramics was obtained. For 3mol% excess of Bi_2O_3 in the mixture of Bi_2O_3-Nb_2O_5 oxides the content of α-$BiNbO_4$ phase was 91wt% and $Bi_5Nb_3O_{15}$ -9wt%. For 5mol% excess of Bi_2O_3 the major phase α-$BiNbO_4$ was in amount of 82 wt % and for 10mol% the phase composition of α-$BiNbO_4$-$Bi_5Nb_3O_{15}$ was 75 wt % – 25 wt %.

Prior to electric measurements the ceramic samples of 1mm in thickness were polished and round-shaped conducting electrodes were deposited on both sides of the disk-shaped ceramics with silver paste.

Knowing the quality of the measured impedance data is essential for a proper analysis. In that connection the Kramers-Kronig relations (K-K) present a very useful tool for data checking [17-22]. Results of the K-K test in the form of the relative difference plots (i.e. relative differences between the measured and calculated value for the real part of impedance and the imaginary part – residuals) for $BiNbO_4$ ceramics with Bi_2O_3 excess have shown that the residuals are either randomly distributed around the $\log(\nu)$ axis or clear traces (the curvatures or oscillations), are present. The random distribution around the frequency axis (Fig. 1*b*) indicates that the data set is K–K compliant [18, 19], whereas a deviation in a form of the curvatures (oscillations) (Fig. 1*a*) shows that there is (minor) non-KK behavior. The data are corrupted by a non steady state behavior. In this case, however, the deviation from K-K behavior is quite small so further analysis of such impedance data is justified and can yield valuable results.



a) *b)*

Fig. 1. K-K test of impedance data for $BiNbO_4$ ceramics with 10mol% of Bi_2O_3 excess sintered at T =870°C and measured at T =RT (*a*) and T =482°C (*b*) (red dots present the real part differences, and the blue dots the imaginary part differences)

The frequency dependent properties of a material are normally described in terms of any of the formalism expressed as complex impedance, complex modulus, complex admittance, complex dielectric permittivity and dielectric losses. One can easily find the exact expressions describing them in literature [e.g. 10, 14, 15 and 19]. It is worth noting however, that these characteristics are interrelated with each other and offer a wide scope for graphical representation. Each representation can be used to highlight a particular aspect of the response of the sample. For example, complex impedance plane plots of Z'' versus Z' are useful for determining the dominant resistance of a sample. However, these are insensitive to smaller resistances. Similarly, complex modulus plots of M'' versus M'

are useful for materials with similar bulk and grain boundary capacitances. The modulus formalism is particularly suitable to extract phenomena such as electrode polarization and conductivity relaxation times [23].

The idealized impedance diagram (Z'' vs. Z'), appears in the form of a succession of semicircles representing electrical phenomena due to bulk material, grain boundary effect and interfacial phenomena if any. When overlapping between processes increases, one may need representations based on combined spectroscopic plots of the imaginary components of impedance, Z'' and electric modulus M'' to reveal the bulk, grain boundary and electrode components of the impedance spectra [24, 25]. Another possible alternative representation of immittance data are possible and are briefly discussed in our previous studies e.g. [14, 15].

In the present research results of immittance measurements are shown in a form of spectroscopic plot of imaginary part of complex impedance (Z'') and imaginary part of complex electric modulus (M'') for $BiNbO_4$ ceramics fabricated with 0%, 3%, 5% and 10% by mole excess of Bi_2O_3 in the initial mixture of oxides Bi_2O_3 –Nb_2O_5 (Fig. 2).

Some oscillations can be seen at the initial part of the measuring frequency range (ν<300 Hz). The noise oscillations decrease for ceramics with 10mol% excess of Bi_2O_3 which may be caused by the better quality of the samples [16].

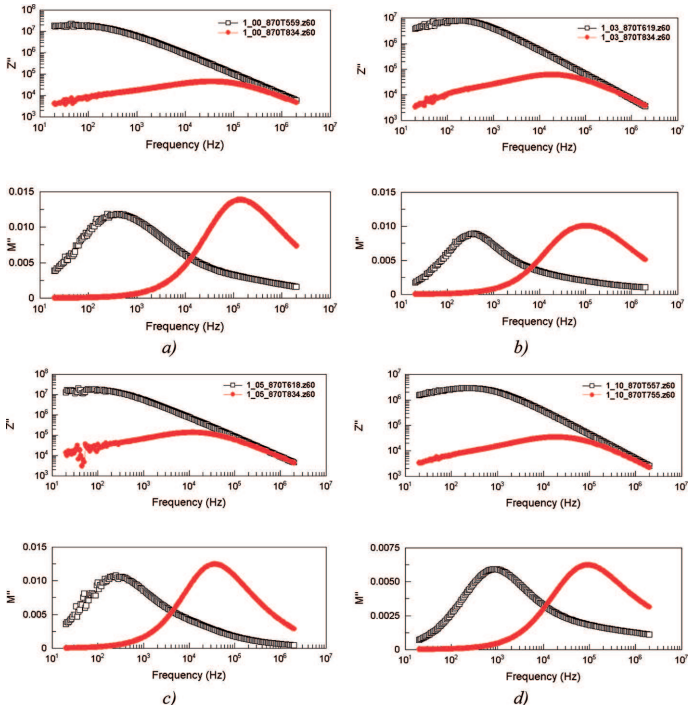


Fig. 2. Spectroscopic plots of imaginary part of complex impedance (Z'') and imaginary part of complex electric modulus (M'') for $BiNbO_4$ ceramics with Bi_2O_3 excess: *a*) – 0 mol%; *b*) – 3 mol%; *c*) – 5mol% and *d*) – 10mol%; @ T>267°C

Dielectric relaxation phenomenon that manifested itself as a maximum on $Z''(\nu)$ curves (highlighted dominant resistive component) appeared in the measuring frequency range only at elevated temperature i.e. T>267°C (Fig. 2). At lower temperatures i.e. below T =267°C, Z'' values fell monotonously with frequency in the frequency range studied for all the compositions, indicating no relaxations in that temperature range.

It can be seen in Fig. 2 that the $Z''(\nu)$ curves display broad peaks with asymmetrical shape. It was found that the Z'' maxima were shifted toward higher frequency with an increase in measuring temperature. At higher frequency, the space charge has lesser time to relax and recombination would be faster. The peak shift was higher for higher temperature. The curves merge above $\nu \approx$100 kHz.

Maxima that appeared on $M''(\nu)$ curves behave in a similar way (bottom plots in Fig. 2), i.e.: (i) the peaks were shifted to higher frequency with increasing temperature; (ii) the peak spreading was increased at higher temperature indicating multiple relaxations; and (iii) the shift in the peak maxima was found to depend on both temperature and Bi content.

One can see in Fig. 3 that value of imaginary part of complex impedance (Z'') first increases with an increase in Bi_2O_3 content and than decreases for 10mol% of additive. An increase in bismuth content up to 5mol% in the initial mixture of Bi_2O_3-Nb_2O_5 oxides caused a shift of the frequency ν_{max} corresponding to maximum of $Z''(\nu)$ and $M''(\nu)$ towards the lower frequency as compared with stoichiometric $BiNbO_4$ ceramics. On the other hand 10mol% of Bi_2O_3 excess in the initial mixture shifted the relaxation frequencies to the higher frequency in relation to stoichiometric $BiNbO_4$ (Fig. 3).

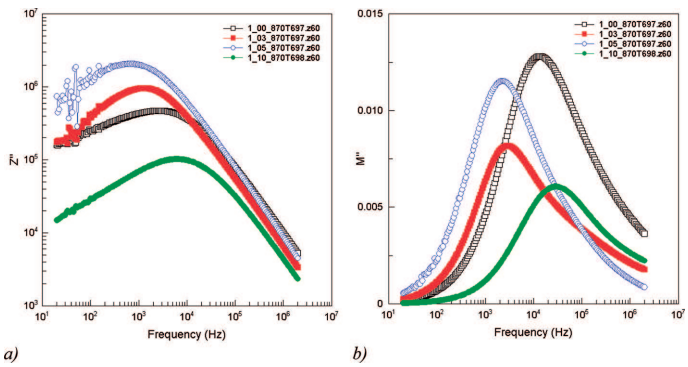


Fig. 3. Influence of bismuth content on spectroscopic plots of $Z''(\nu)$(*a*) and $M''(\nu)$ (*b*) for $BiNbO_4$ ceramics at $T \approx$425°C

In case of the ideal Debye type relaxation (i.e. for a particular *RC* combination) $Z''(\nu)$ and $M''(\nu)$peaks should be coincident on the frequency scale. However, the comparison of $Z''(\nu)$ and $M''(\nu)$ spectra shows that $Z''(\nu)$ peaks do not coincide with the peak in $M''(\nu)$ (Fig. 4). The peak in $Z''(\nu)$ is slightly shifted to lower frequency with respect to $M''(\nu)$ peak position for all measured samples. Therefore, one can suppose the presence of overlapped dielectric relaxation processes in $BiNbO_4$ ceramics that manifested themselves within the measuring frequency range and temperature range. Also the widths of the peaks suggest a spread of relaxation times, which may involve more than two equilibrium positions.

Taking into account that an increase in the amount of Bi_2O_3 compound in the initial mixture of oxides Bi_2O_3-Nb_2O_5 caused, apart from major $BiNbO_4$ phase, a formation and an increase in the weight percentage of the tetragonal $Bi_5Nb_3O_{15}$ phase one can conclude that both phases contribute to the dielectric response of the resultant ceramics.

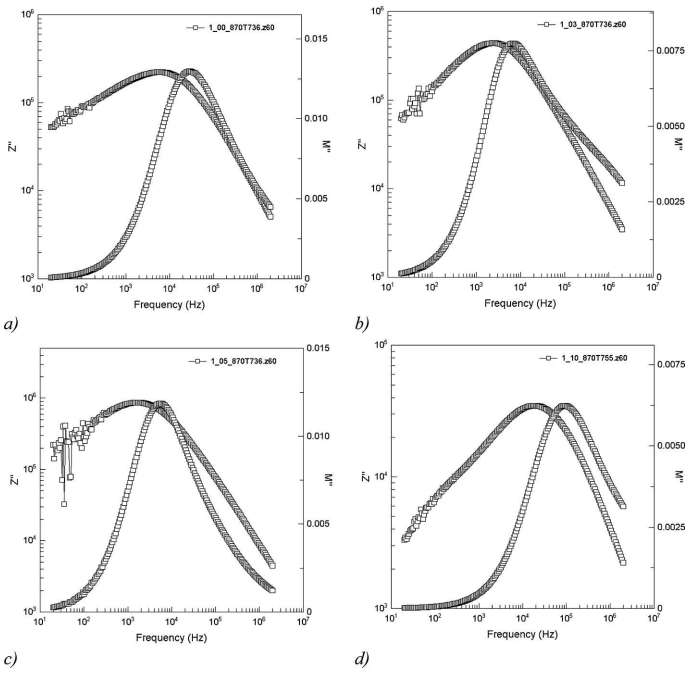


Fig. 4. Combined plots of $Z''(\nu)$ and$M''(\nu)$ spectra showing lack of coincidence of maxima on the frequency scale at $T \approx 463$°C for $BiNbO_4$ ceramics: *a*) – 0 mol%; *b*) – 3 mol%; *c*) – 5mol% and *d*) – 10mol% of Bi_2O_3 excess

To confirm thermal activation of the revealed relaxation processes (Fig. 2 – Fig. 4) the Arrhenius relation was employed. Using linear regression, the activation energy corresponding to non-Debye type of relaxation has been calculated from $Z''(\nu)$ spectrum. The conductivity relaxation parameters associated with the high disorder charge conduction [14, 23] have been determined from $M''(\nu)$ spectrum. Values of the calculated activation energies (E_A) of relaxation times (τ) and pre-exponential factor (τ_0) of the relaxation time are given in Tab. 1.

TABLE 1
Activation energy of the relaxation time and pre-exponential factor calculated from $Z''(\nu)$ and $M''(\nu)$ spectra according to Arrhenius relation

Phase composition; $BiNbO_4/Bi_5Nb_3O_{15}$; wt%	Derived from$Z''(\nu)$		Derived from$M''(\nu)$	
	E_A; [eV]	τ_0, [s]	E_A; [eV]	τ_0, [s]
100/0	0.95	8.85×10^{-12}	0.85	8.20×10^{-12}
91/ 9	0.95	1.72×10^{-11}	1.12	3.81×10^{-13}
82/18	1.04	6.52×10^{-12}	1.02	2.74×10^{-12}
75/25	0.81	3.15×10^{-11}	0.89	1.67×10^{-12}

One can see from Tab. 1 that the phase composition of the resultant ceramics has a little effect on value of activation energy. However, an increase in amount of minor tetragonal $Bi_5Nb_3O_{15}$ phase, caused by Bi_2O_3 excess in amount of 3mol% and 5mol% in the initial mixture of oxides, results in a small increase in activation energy. Further increase in $Bi_5Nb_3O_{15}$ amount corresponding to 10mol% excess of Bi_2O_3 caused a decrease in the activation energy. Such dependence can bee seen for both $Z''(\nu)$ and $M''(\nu)$ derived relaxation parameters. Value of activation energies obtained from the analyses of $Z''(\nu)$ and $M''(\nu)$ data suggests that the transport is through ion hopping mechanism in the investigated $BiNbO_4$ ceramics [23]. Therefore, it is reasonably suppose that one mechanism of the revealed relaxation processes is present in $BiNbO_4$ ceramics however, substantial distribution of relaxation times due to multiphase composition takes place.

4. Conclusion

Dielectric behavior of α-phase $BiNbO_4$ ceramics modified with an excess of 0%, 3%, 5% and 10% by mole of Bi_2O_3 and sintered at T_S =870°C has been studied as a function of temperature and frequency. It was found that resultant $BiNbO_4$ ceramics was multiphase with the presence of minor $Bi_5Nb_3O_{15}$ phase. An amount of the minor phase corresponding to 5mol% of Bi_2O_3 excess has decreased dielectric losses of the material under study within the measuring frequency range (ν =20Hz-1MHz) and temperature changes (T =RT-550°C)

The relaxation phenomena were revealed at elevated temperature (T>267°C) within the measuring frequency range. The process with dominant resistive component ($Z''(\nu)$ spectra) took place at lower frequency than the conductivity relaxation phenomenon ($M''(\nu)$ spectra). The change of Z'' and M'' for unit frequency interval was found to depend on temperature and concentration of bismuth in the resultant $BiNbO_4$ ceramics. The broadening of the peaks and half-widths of the peaks indicated multiple relaxations and deviations from Debye behavior.

Activation energy of the relaxation times describing relaxation of polarization phenomena (Z'') and conductivity relaxation (M'') were calculated. The near value of activation energies obtained from the analyses of Z'' and M'' data confirms that the transport is through ion hopping mechanism in the investigated materials. Thermal activation of the revealed relaxation processes was confirmed however, additional studies based on equivalent circuit method [10, 14] with the complex non-linear least squares simulation technique [26] are necessary to get better view on contribution of particular phases present in $BiNbO_4$ resultant ceramics into total dielectric response.

Acknowledgements

The present research has been supported by Polish National Science Centre (NCN) from the funds for science in 2011-2014 as a research project N N507 218540. Authors acknowledge Dr K.Osińska for the samples fabrication.

REFERENCES

[1] 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).

[2] 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).

[3] 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 di-

electric properties of $BiNbO_4$ ceramics, Journal Of Materials Science **35**, 5443-5447 (2000).

[4] S.K. K o, K.Y. K i m, B.H. K i m, Characteristics of tapped microstrip bandpass filter in $BiNbO_4$ ceramics, Journal of Materials Science: Materials in Electronics **9**, 351-356 (1998).

[5] 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).

[6] 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).

[7] 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).

[8] 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 20^{th} Annual International Conference on Composites or Nano Engineering ICCE-20, Beijing, China, 2012.

[9] 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).

[10] E. B a r s u k o v, J. R o s s M a c d o n a l d (Red)., Impedance spectroscopy, theory, experiment, and applications, John Willey & Sons, Inc., Hoboken, New Jersey, (2005).

[11] W. B o g u s z, F. K r o k, Elektrolity stałe. Właściwości elektryczne i sposoby ich pomiaru, WNT, Warszawa (1995); K.Nitsch, Zastosowanie spektroskopii impedancyjnej w badaniach materiałów elektronicznych, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław (1999).

[12] A.R. W e s t, D.C. S i n c l a i r, N. H i r o s e, Characterization of electrical materials, especially ferroelectrics, by impedance spectroscopy, Journal of Electroceramics, **1**, 1, 65-71 (1997).

[13] E.J. A b r a m, D.C. S i n c l a i r, A.R. W e s t, A Strategy for Analysis and Modelling of Impedance Spectroscopy Data of Electroceramics: Doped Lanthanum Gallate, Journal of Electroceramics **10**, 165-177 (2003).

[14] A. L i s i ń s k a - C z e k a j, Wielofunkcyjne materiały na osnowie tytanian bizmutu, Uniwersytet Śląski, Wydawnictwo Gnome, Katowice, 2012.

[15] D. C z e k a j, Fabrication and study of BST-based functional materials, Uniwersytet Śląski, Wydawnictwo Gnome, Katowice, 2010.

[16] 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.

[17] 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).

[18] B.A. B o u k a m p, A linear Kronig-Kramers transform test for immitance data validation, J. Electrochem. Soc. **142**, 1885-1894 (1995).

[19] 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).

[20] 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_2O_3-Nb_2O_5, Bi_2O_3-Ta_2O_5, Bi_2O_3-MoO_3, and Bi_2O_3-WO_3, Journal of Solid State Chemistry **137**, 42-61 (1998).

[21] MATCH! Version 2.1.2, CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany (URL: http://www.crystalimpact.com/match).

[22] A. L i s i ń s k a - C z e k a j, B. W o d e c k a - D u ś, D. C z e k a j, Application of ac impedance spectroscopy for characterization of $BiNbO_4$ ceramics, Key Engineering Materials **512-515**, 1193-1197 (2012).

[23] P.S. A n a n t h a, K. H a r i h a r a n, AC conductivity analysis and dielectric relaxation behaviour of $NaNO_3$-$Al2O_3$ composites, Materials Science and Engineering B **121**, 12-19 (2005).

[24] D.C. S i n c l a i r, A.R. W e s t, Impedance and modulus spectroscopy of semiconducting $BaTiO_3$ showing positive temperature coefficient of resistance, J.Appl. Phys. *66*, 3850-3856 (1989).

[25] J.T.S. I r v i n e, D.C. S i n c l a i r, A.R. W e s t, Electroceramics: characterization by impedance spectroscopy, Adv. Mater. **2**, 132-138 (1990).

[26] B. B o u k a m p, A nonlinear least squares fit procedure for analysis of immittance data of electrochemical systems, Solid State Ionics **20**, 31-44 (1986).

Received: 10 April 2013.