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**Title:** Influence of bismuth content on complex immittance characteristics of pressureless sintered BiNbO<sub>4</sub> ceramics

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**INFLUENCE OF BISMUTH CONTENT ON COMPLEX IMPEDANCE CHARACTERISTICS OF PRESSURELESS SINTERED  $\text{BiNbO}_4$  CERAMICS****WPLYW ZAWARTOŚCI BIZMUTU NA ZESPOLONE CHARAKTERYSTYKI IMMITANCYJNE SPIEKANEJ SWOBODNIE CERAMIKI  $\text{BiNbO}_4$** 

Goal of the present research was to study impedance properties of  $\text{BiNbO}_4$  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.  $\text{Bi}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  as well as the ones with an excess of 3%, 5% and 10% by mole of  $\text{Bi}_2\text{O}_3$ . The impedance properties were studied by impedance spectroscopy. Measurements were carried out within the frequency range  $\nu = 20\text{Hz}-1\text{MHz}$  and temperature range  $T = \text{RT}-550^\circ\text{C}$ . 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  $\text{Bi}_2\text{O}_3$  content and decreases for 10mol% excess of  $\text{Bi}_2\text{O}_3$ . Two relaxation phenomena manifested themselves at elevated temperature ( $T > 267^\circ\text{C}$ ) 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:*  $\text{BiNbO}_4$  ceramics, impedance spectroscopy, impedance and modulus analysis

Celem niniejszej pracy było zbadanie właściwości immitancyjnych ceramiki  $\text{BiNbO}_4$  wytworzonej metodą reakcji w fazie stałej i spiekania swobodnego. Badaniom poddano cztery zestawy próbek wytworzonych ze stechiometrycznej mieszaniny tlenków  $\text{Bi}_2\text{O}_3$  i  $\text{Nb}_2\text{O}_5$  oraz mieszaniny zawierającej nadmiar  $\text{Bi}_2\text{O}_3$  w ilości 3, 5 i 10% molowych. Badania przeprowadzono z zastosowaniem spektroskopii impedancyjnej. Pomiarów dokonano w zakresie częstotliwości  $\nu = 20\text{Hz}-1\text{MHz}$  i temperatury  $T = \text{RT}-550^\circ\text{C}$ . Do analizy zgodności danych pomiarowych zastosowano test Kramersa-Kroniga. Stwierdzono, że ze wzrostem zawartości  $\text{Bi}_2\text{O}_3$  w mieszaninie do 5% molowych wzrasta impedancja próbek, która dla 10% molowych maleje poniżej wartości zarejestrowanej dla  $\text{BiNbO}_4$  bez nadmiaru  $\text{Bi}_2\text{O}_3$ . Zaobserwowano obecność dwóch procesów relaksacyjnych w temperaturze  $T > 267^\circ\text{C}$ . 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 ( $\text{BiNbO}_4$ ) has been reported to be a promising microwave dielectric ceramics [1, 2] To improve the microwave dielectric properties of  $\text{BiNbO}_4$  various attempts have been undertaken. Among them one can mention e.g. addition of various sintering aids like a small amount of  $\text{CuO}$  and  $\text{V}_2\text{O}_5$  [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  $\text{Bi}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  or  $\text{Bi}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$  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  $\text{Bi}_2\text{O}_3$  was added to fabricate  $\alpha$ -phase  $\text{BiNbO}_4$  ceramics. However, the effect of  $\text{Bi}_2\text{O}_3$  excess and sintering temperature on low frequency dielectric characteristics of  $\alpha$ -phase  $\text{BiNbO}_4$  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  $\text{BiNbO}_4$  dielectric. Therefore in the present paper  $\text{BiNbO}_4$  ceramics were chosen as a host material to be sintered with an excess of  $\text{Bi}_2\text{O}_3$  at  $T_S = 870^\circ\text{C}$ . The basic dielectric properties were analyzed based on the phase composition of the  $\text{BiNbO}_4$  ceramics derived from bismuth-rich  $\text{Bi}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$  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

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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<sub>4</sub> ceramics were prepared by the conventional mixed oxide method from the mixture of oxide powders, viz. Bi<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub>. However, apart from the stoichiometric composition of powders an excess of 3%, 5% and 10% by mole of Bi<sub>2</sub>O<sub>3</sub> has been used to prepare green bodies. Details of the preparation method have been reported by us elsewhere [8, 9]. Also the sintered BiNbO<sub>4</sub> 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  $\nu = 20\text{Hz}-1\text{MHz}$  and temperature range  $T = \text{RT}-550^\circ\text{C}$ . 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 ( $\alpha$ -BiNbO<sub>4</sub> compound) with the lattice parameters differing slightly ( $\pm 0.02\%$ ) with Bi<sub>2</sub>O<sub>3</sub> excess. It was also found that BiNbO<sub>4</sub> ceramics fabricated from bismuth-rich Bi<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub> system exhibited the multiphase composition, i.e. apart from major  $\alpha$ -BiNbO<sub>4</sub> phase a small amount of additional phases like Bi<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub>, and Bi<sub>3</sub>NbO<sub>7</sub> was detected [16]. Therefore, to correlate the results of the dielectric measurements with the actual phase composition of fabricated BiNbO<sub>4</sub> ceramics the assumption was made that ceramics under study consists of two phases, namely orthorhombic  $\alpha$ -BiNbO<sub>4</sub> phase and tetragonal Bi<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub> phase, what in turn is consistent with the published phase diagrams of Bi<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub> 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<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub> (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<sub>2</sub>O<sub>3</sub> in the mixture of Bi<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub> oxides the content of  $\alpha$ -BiNbO<sub>4</sub> phase was 91wt% and Bi<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub> -9wt%. For 5mol% excess of Bi<sub>2</sub>O<sub>3</sub> the major phase  $\alpha$ -BiNbO<sub>4</sub> was in amount of 82 wt % and for 10mol% the phase composition of  $\alpha$ -BiNbO<sub>4</sub>-Bi<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub> 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<sub>4</sub> ceramics with Bi<sub>2</sub>O<sub>3</sub> 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. 1b) indicates that the data set is K-K compliant [18, 19], whereas a deviation in a form of the curvatures (oscillations) (Fig. 1a) 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.

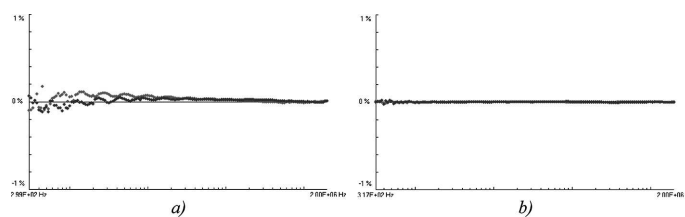


Fig. 1. K-K test of impedance data for BiNbO<sub>4</sub> ceramics with 10mol% of Bi<sub>2</sub>O<sub>3</sub> excess sintered at  $T = 870^\circ\text{C}$  and measured at  $T = \text{RT}$  (a) and  $T = 482^\circ\text{C}$  (b) (red dots present the real part differences, and the blue dots the imaginary 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  $\text{BiNbO}_4$  ceramics fabricated with 0%, 3%, 5% and 10% by mole excess of  $\text{Bi}_2\text{O}_3$  in the initial mixture of oxides  $\text{Bi}_2\text{O}_3 - \text{Nb}_2\text{O}_5$  (Fig. 2).

Some oscillations can be seen at the initial part of the measuring frequency range ( $\nu < 300$  Hz). The noise oscillations decrease for ceramics with 10mol% excess of  $\text{Bi}_2\text{O}_3$  which may be caused by the better quality of the samples [16].

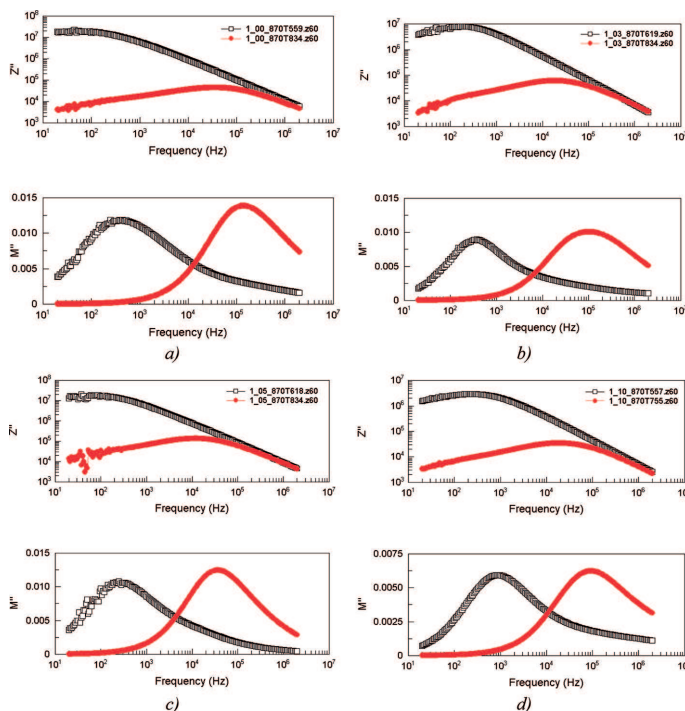


Fig. 2. Spectroscopic plots of imaginary part of complex impedance ( $Z''$ ) and imaginary part of complex electric modulus ( $M''$ ) for  $\text{BiNbO}_4$  ceramics with  $\text{Bi}_2\text{O}_3$  excess: a) – 0 mol%; b) – 3 mol%; c) – 5mol% and d) – 10mol%; @  $T > 267^\circ\text{C}$

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.  $T > 267^\circ\text{C}$  (Fig. 2). At lower temperatures i.e. below  $T = 267^\circ\text{C}$ ,  $Z''$  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  $\text{Bi}_2\text{O}_3$  content and then decreases for 10mol% of additive. An increase in bismuth content up to 5mol% in the initial mixture of  $\text{Bi}_2\text{O}_3 - \text{Nb}_2\text{O}_5$  oxides caused a shift of the frequency  $\nu_{max}$  corresponding to maximum of  $Z''(\nu)$  and  $M''(\nu)$  towards the lower frequency as compared with stoichiometric  $\text{BiNbO}_4$  ceramics. On the other hand 10mol% of  $\text{Bi}_2\text{O}_3$  excess in the initial mixture shifted the relaxation frequencies to the higher frequency in relation to stoichiometric  $\text{BiNbO}_4$  (Fig. 3).

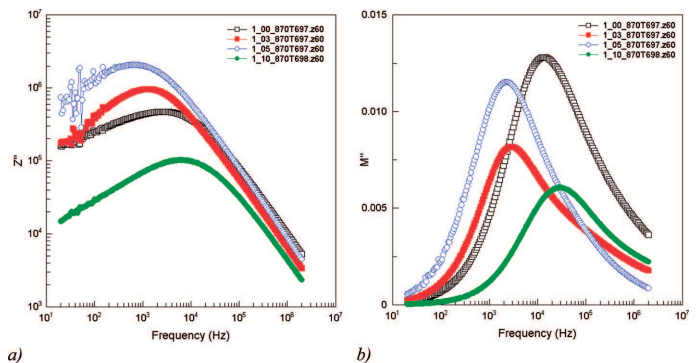


Fig. 3. Influence of bismuth content on spectroscopic plots of  $Z''(\nu)$ (a) and  $M''(\nu)$  (b) for  $\text{BiNbO}_4$  ceramics at  $T \approx 425^\circ\text{C}$

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  $\text{BiNbO}_4$  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  $\text{Bi}_2\text{O}_3$  compound in the initial mixture of oxides  $\text{Bi}_2\text{O}_3 - \text{Nb}_2\text{O}_5$  caused, apart from major  $\text{BiNbO}_4$  phase, a formation and an increase in the weight percentage of the tetragonal  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  phase one can conclude that both phases contribute to the dielectric response of the resultant ceramics.

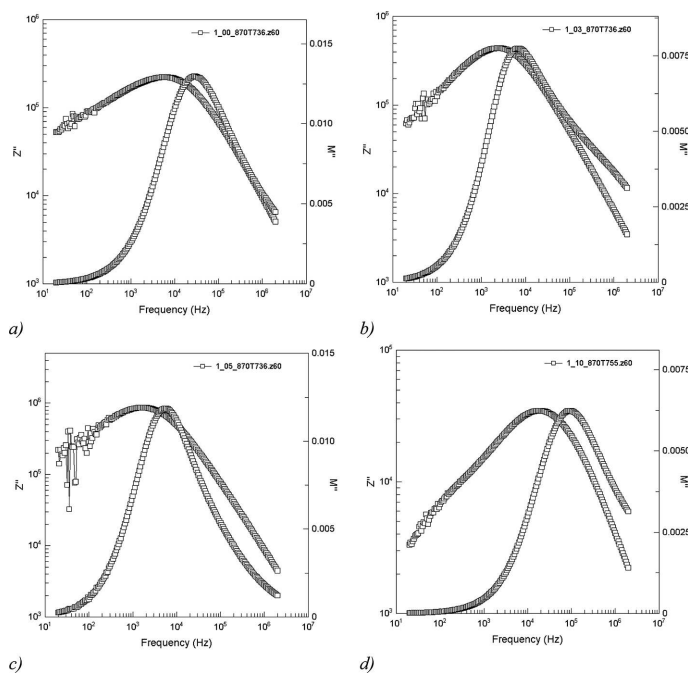


Fig. 4. Combined plots of  $Z''(\nu)$  and  $M''(\nu)$  spectra showing lack of coincidence of maxima on the frequency scale at  $T \approx 463^\circ\text{C}$  for  $\text{BiNbO}_4$  ceramics: a) – 0 mol%; b) – 3 mol%; c) – 5 mol% and d) – 10 mol% of  $\text{Bi}_2\text{O}_3$  excess

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 ( $\tau$ ) and pre-exponential factor ( $\tau_0$ ) 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; $\text{BiNbO}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ ; wt%	Derived from $Z''(\nu)$		Derived from $M''(\nu)$	
	$E_A$ ; [eV]	$\tau_0$ , [s]	$E_A$ ; [eV]	$\tau_0$ , [s]
100/0	0.95	$8.85 \times 10^{-12}$	0.85	$8.20 \times 10^{-12}$
91/ 9	0.95	$1.72 \times 10^{-11}$	1.12	$3.81 \times 10^{-13}$
82/18	1.04	$6.52 \times 10^{-12}$	1.02	$2.74 \times 10^{-12}$
75/25	0.81	$3.15 \times 10^{-11}$	0.89	$1.67 \times 10^{-12}$

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  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  phase, caused by  $\text{Bi}_2\text{O}_3$  excess in amount of 3 mol% and 5 mol% in the initial mixture of oxides, results in a small increase in activation energy. Further increase in  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  amount corresponding to 10 mol% excess of  $\text{Bi}_2\text{O}_3$  caused a decrease in the activation energy. Such dependence can be 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  $\text{BiNbO}_4$  ceramics [23]. Therefore, it is reasonable to suppose that one mechanism of the revealed relaxation processes is present in  $\text{BiNbO}_4$  ceramics however, substantial distribution of relaxation times due to multiphase composition takes place.

#### 4. Conclusion

Dielectric behavior of  $\alpha$ -phase  $\text{BiNbO}_4$  ceramics modified with an excess of 0%, 3%, 5% and 10% by mole of  $\text{Bi}_2\text{O}_3$  and sintered at  $T_S = 870^\circ\text{C}$  has been studied as a function of temperature and frequency. It was found that resultant  $\text{BiNbO}_4$  ceramics was multiphase with the presence of minor  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  phase. An amount of the minor phase corresponding to 5 mol% of  $\text{Bi}_2\text{O}_3$  excess has decreased dielectric losses of the material under study within the measuring frequency range ( $\nu = 20\text{Hz} - 1\text{MHz}$ ) and temperature changes ( $T = \text{RT} - 550^\circ\text{C}$ ).

The relaxation phenomena were revealed at elevated temperature ( $T > 267^\circ\text{C}$ ) 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  $\text{BiNbO}_4$  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  $\text{BiNbO}_4$  resultant ceramics into total dielectric response.

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