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A NEW MICROWAVE CERAMIC – POLYMER COMPOSITE WITH 0-3 CONNECTIVITY

NOWY KOMPOZYT CERAMICZNO – POLIMEROWY O SPOSOBIE ŁĄCZENIA FAZ 0-3

Goal of the present research was to fabricate and study two-phase $BiNbO_4$//PVDF composites with 0-3 connectivity. Such composite consists of there-dimensionally connected polymer matrix loaded with dielectric ceramic particles. In the present case $BiNbO_4$ powder acted as an active phase (dispersed phase) whereas polyvinylidene fluoride (PVDF) acted as a non-active (passive) phase (matrix). $BiNbO_4$//PVDF composites with the volume fraction of the ceramic phase c_V =2, 4, 6, 8, 10, 16 and 20 vol. % were prepared. Average grain size of $BiNbO_4$ powder was $<d>$=1.86 μm. It was found that $BiNbO_4$ powder exhibited orthorhombic symmetry with *Pnna* (52) space group and PVDF polymer powder was α-phase. Minimum of dielectric losses at room temperature were found within the frequency range $\Delta\nu$ =10^3-10^4 Hz. It was found that composite with c_V =10% of ceramic powder exhibited lower values of dielectric permittivity.
Keywords: $BiNbO_4$, microwave ceramics, PVDF, ceramic-polymer composite, 0-3 connectivity, dielectric properties

Celem niniejszej pracy było wytworzenie i zbadanie wybranych właściwości kompozytu dwufazowego $BiNbO_4$//PVDF o sposobie łączenia faz 0-3. Taki kompozyt zbudowany jest z trójwymiarowo połączonej osnowy polimerowej wypełnionej dielektrycznymi cząsteczkami ceramicznymi. W badanym kompozycie proszek $BiNbO_4$ pełnił rolę aktywnej fazy dielektrycznej (faza rozproszona), podczas gdy poli(fluorek winylidenu) (PVDF) pełnił rolę fazy nieaktywnej (osnowy). W toku pracy przygotowano kompozyty $BiNbO_4$//PVDF o zawartości fazy ceramicznej c_V =2, 4, 6, 8, 10, 16 i 20% i średnim rozmiarze cząsteczek dyspergowanych $<d>$=1,86 μm. Stwierdzono, że ceramika $BiNbO_4$ wykazuje symetrię rombową *Pnna*(52) natomiast wykorzystany polimer krystalizował w fazie α. Badanie właściwości dielektrycznych w temperaturze pokojowej pozwoliło określić zakres częstotliwości $\Delta\nu$ =10^3-10^4 Hz, którym występuje minimum strat dielektrycznych. Stwierdzono, że kompozyt zawierający c_V =10% proszku $BiNbO_4$ wykazuje najmniejsze wartości przenikalności elektrycznej.

1. Introduction

Microwave dielectric ceramic (MWDC) is becoming the key fundamental material for mobile communication technique and widely used in military and civilian communication systems. Currently, the development and application research of low and high permittivity MWDC are much more advanced than those of the middle ones. Most of middle permittivity MWDCs are focused on ceramics with ε_r<40, such as, (Zr,Sn)TiO_4, $BiNbO_4$ and ceramics based on BaO-TiO_2 system [1].

In the present research $BiNbO_4$ ceramics were under study and the composite technology was utilized. Composites that are constituted from ceramics and polymer have gained a widespread application in a number of electromechanical transducers. Properties of composites are known to be determined by the number of phases, the volumetric fraction, properties of individual phases and by the way in which the different phases are interconnected. The simplest type of the composites is that with 0-3 connectivity. Such a composite consists of the there-dimensionally connected polymer matrix loaded with ceramic particles. In 0-3 connectivity the ceramic particles are not in contact with each other and the polymer phase is self-connected in all directions [2, 3].

The main goal of the present research was to develop ceramic-polymer composites based on prospective microwave ceramics and poly(vinylidene fluoride) polymer $BiNbO_4$//PVDF. Attention was confined to one of the most commonly encountered connectivity 0-3. The composites should differ in concentration of ceramic phase expressed in volumetric percentage c_V =2, 4, 6, 8, 10, 16 and 20%, so that influence of ceramic phase on structure and dielectric properties of ceramic-polymer composite with different volume fraction of the ceramic reinforcement would be revealed.

2. Experimental

$BiNbO_4$ powder was prepared by the mixed oxide method from mixture of oxides: Bi_2O_3 and Nb_2O_5. Green bodies in a form of disks of diameter φ =25mm were subjected to synthesis (T =800°C t =2h) and subsequent heat treatment at T =960°C for t =2h. Details of fabrication of $BiNbO_4$ ce-

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ramics were given by us elsewhere [4, 5]. However, it should be noted that $BiNbO_4$ ceramics was eventually crumbled and powdered in a planetary ball mill. Thus obtained $BiNbO_4$ powder was then used for composite fabrication.

The $BiNbO_4$//PVDF ceramic-polymer composites were fabricated by the "hot pressing method" [6, 7]. $BiNbO_4$ and PVDF powders were first thoroughly weighted and mixed so volume fraction of the ceramic phase was c_V =2, 4, 6, 8, 10, 16 and 20 vol%. After homogenization the ceramic-polymer mixture was heated in a steel die up to T =165°C, pressed at p =120MPa and cooled down to room temperature under pressure in ambient air atmosphere.

Thus obtained $BiNbO_4$//PVDF composites were characterized in terms of their crystalline structure and dielectric properties. Crystalline structure of $BiNbO_4$//PVDF composites was studied by the X-ray diffraction method (XPert-Pro diffractometer, Θ-2Θ mode, CuKα radiation).

For electric measurements, composite samples of 1 mm thick and 20 mm in diameter were covered with silver paste electrodes. The frequency dependence of complex dielectric permittivity of $BiNbO_4$//PVDF composites was measured in the frequency range of f =1kHz-1MHz at room temperature.

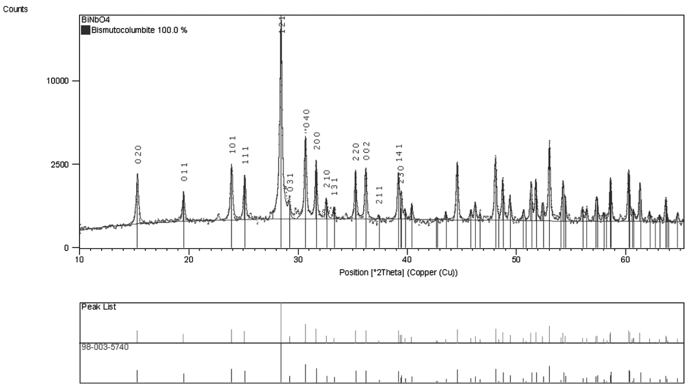

Fig. 2. X-ray diffraction pattern of $BiNbO_4$ powder heat-treated at T =960°C

The $BiNbO_4$//PVDF ceramic-polymer composites were fabricated from $BiNbO_4$ powder and PVDF powder mixed in proportions given in Tab. 1. Apparent density of the composite samples is given in Fig. 3.

TABLE 1

Composition of composites

c_V [%]	2	4	6	8	10	16	20
$BiNbO_4$ [g]	0.295	0.590	0.885	1.181	1.476	2.362	2.952
PVDF [g]	5.174	5.068	4.963	4.857	4.752	4.435	4.224

3. Results and discussions

Grain size distribution of $BiNbO_4$ powder was measured with Mastersizer-type laser meter. The cumulative curve of material passing is given in Fig. 1. One can see that two-mode distribution was obtained. First modal value was d =0.23μm and the second modal value was d =2.3 μm. Calculated average grain size was<d>=1.86 μm (Fig. 1).

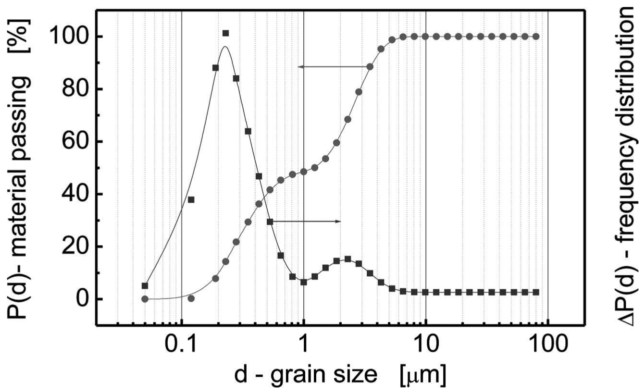

Fig. 1. Grain size distribution of $BiNbO_4$ powder

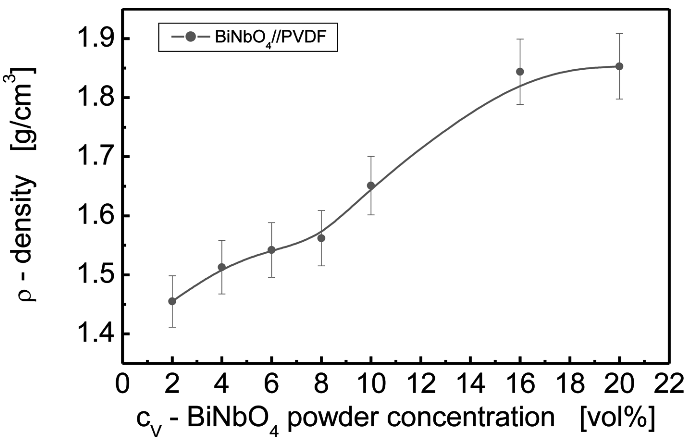

Fig. 3. Apparent density of $BiNbO_4$//PVDF composites

X-ray diffraction pattern of $BiNbO_4$ powder is given in Fig. 2. It was found that the powder exhibited orthorhombic symmetry with *Pnna* (52) space group. Parameters of the elementary cell were as follows: a =5.6796(2) Å, b =11.7114(4) Å and c =4.9819(2) Å. In this connection it should be added that refinement of the elementary cell parameters was performed on the base of a model crystal structure of α-$BiNbO_4$ given in the crystallographic information file with the ISCD code 74338 (PDF-00-016-0295).

PVDF is a semi-crystalline polymer presenting a complex structure with four possible crystalline phases [8]. For PVDF, the first strong diffraction peaks at about 2θ =17.9, 18.4 and 20.1^0 are the distinctive feature of α-phase of PVDF, which are attributed to the (100), (020) and (110) reflections, respectively. (Fig. 4; PDF code of the model crystal structure: 421650).

One can see from Fig. 5 that with an increase in $BiNbO_4$ content intensity of X-ray diffraction peaks of PVDF polymer in composite samples decreases.

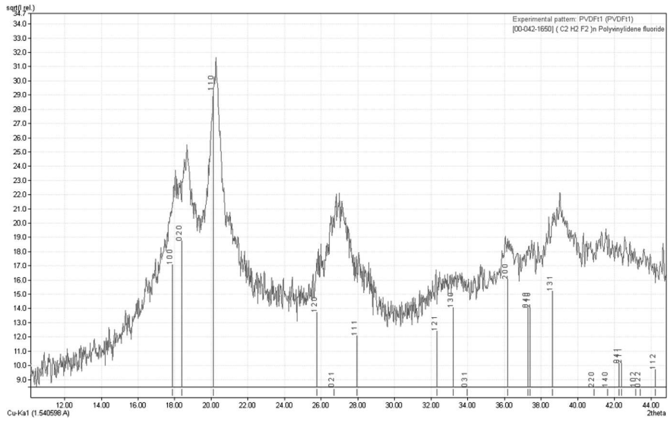

Fig. 4. X-ray diffraction pattern for PVDF polymer used in the present study together with diffraction lines of PVDF model structure (code 421650)

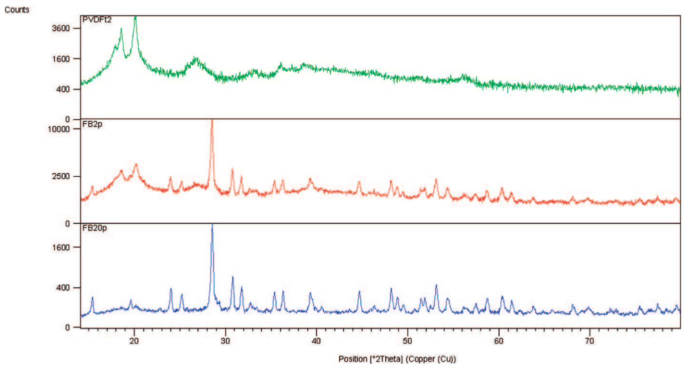

Fig. 5. Comparison of X-ray diffraction patterns for PVDF (upper plot) and $BiNbO_4$//PVDF composites containing c_V =2vol% and 20vol% of ceramic phase (middle and bottom plot, respectively)

Dielectric spectroscopic measurements for $BiNbO_4$//PVDF composites containing c_V =2-20vol% of ceramic powder were performed at room temperature. One can see from Fig. 6*a*) that real part of dielectric permittivity decreases with an increase in frequency of the measuring field. However, the dependence (Fig. 6*a*) exhibited two negative slopes in a log-log scale, first within the frequency range $\Delta\nu$ =100Hz-100 kHz and second at higher frequency range, namely $\Delta\nu$ =10^5-10^6 Hz. Imaginary part of dielectric permittivity (i.e. dielectric loss factor) exhibited a local minimum within the frequency range $\Delta\nu$ =10^3-10^4 Hz. No shift of the local minimum (at $\nu \approx 5$ kHz for all studied samples) was observed with an increase in $BiNbO_4$ powder concentration (Fig. 6*b*). One can see from Fig. 6 that absolute value of real and imaginary components of dielectric permittivity progressively increase with an increase in dispersed phase concentration to reach a maximal value at c_V =8vol%. It is worth noting that for frequency ν>3kHz the spectroscopic plots registered for composites with c_V =6vol% and c_V =8vol% of $BiNbO_4$ powder were almost identical so a kind of "saturation" effect took place.

Further increase in amount of $BiNbO_4$ powder to c_V =10vol% caused an unexpected decrease in dielectric permittivity and dielectric loss factor. As a result the lowest observed values of real and imaginary parts of dielectric permittivity were obtained for $BiNbO_4$//PVDF composite with c_V =10% of $BiNbO_4$ powder. Additional increase in amount of $BiNbO_4$ powder in amount of c_V =16 and 20vol% caused another increase in values of components of the complex dielectric permittivity. Nevertheless, the highest values that had been registered for composite with c_V =8vol% were not reached.

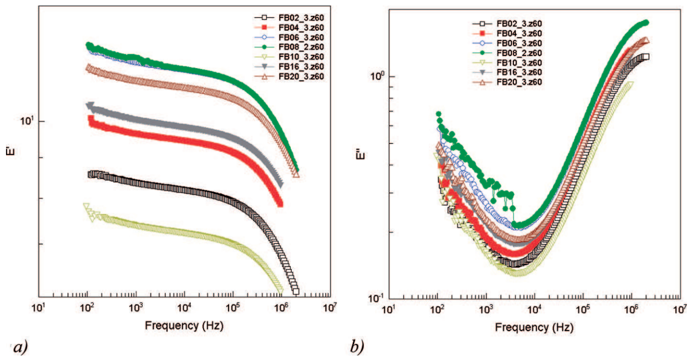

Fig. 6. Spectroscopic plots of real (*a*) and imaginary (*b*) parts of dielectric permittivity for $BiNbO_4$//PVDF composites containing c_V =2- 20vol% of $BiNbO_4$ powder

Such non-monotonic dependence of the real and imaginary parts of complex dielectric permittivity of the $BiNbO_4$//PVDF composites on the dispersed phase concentration with a local minimum at c_V =10vol% can be discussed from the point of view of the distribution of ceramic particles in the polymer matrix.

X-ray diffraction phase analysis was performed for $BiNbO_4$//PVDF composites with Match! (Crystal Impact) computer program [9]. Model structures described in PDF cards No 160295 and No 421650 were taken as $BiNbO_4$ phase and PVDF phase respectively. As far as the model structures available did not contain reference intensity ratio information the default value of I/I_C =1 was used for calculations. The results showed that for $BiNbO_4$//PVDF composite with $c_V \geqslant$10vol% of ceramic powder the weight fraction of $BiNbO_4$ is 100%.

The Authors realize that the calculations performed were not precise due to the lack of the required I/I_C parameter for both phases. However, even the approximate results showed that it was likely to exceed the percolation threshold in the composites or disturb the distribution of the ceramic particles in such a way that 0-3 connectivity was not longer valid for concentration of dispersed phase $c_V \geqslant$10vol%.

Electric equivalent circuit method was used to model the dielectric response of prepared composites. It is commonly known [e.g. 10, 11] that the elements of an equivalent circuit model represent the various (macroscopic) processes involved in the transport of mass and charge. Equivalent circuit used for impedance spectroscopy data simulation in the present study was composed of a series combination of two parallel combinations of a resistance R and a constant phase element CPE (see inset in Fig. 7). In solid materials, a distribution of relaxation times is usually observed and the capacitance is replaced by a CPE, which represents more accurately the behavior of the grain interior, grain boundary and electrode processes [11, 12].

After deconvolution of impedance parameters obtained with the data shown in Fig. 6 the time constants τ_1 and τ_2 corresponding to the parallel RC elements (calculation of capacitance was performed from CPE element parameters according to the method given elsewhere [e.g. 12, 11]) constituting the resultant equivalent circuit were calculated and plotted as a function of dispersed phase concentration in Fig. 7. The results illustrate that two different relaxation processes took place in $BiNbO_4$//PVDF composites at room temperature. Standard deviation for the relaxation times was calculated (error bars in Fig. 7) and the assumption was made that the dependence of relaxation time on concentration of the dispersed phase was linear. One can see in Fig. 7 that linear regression in semi-log scale shows that the relaxation times τ_1 and τ_2 are almost invariant on concentration of $BiNbO_4$ powder but they are separated for 5 orders of magnitude, i.e. $\tau_1 = 5.1\times10^{-2}$ s and $\tau_2 = 2.7\times10^{-7}$ s.

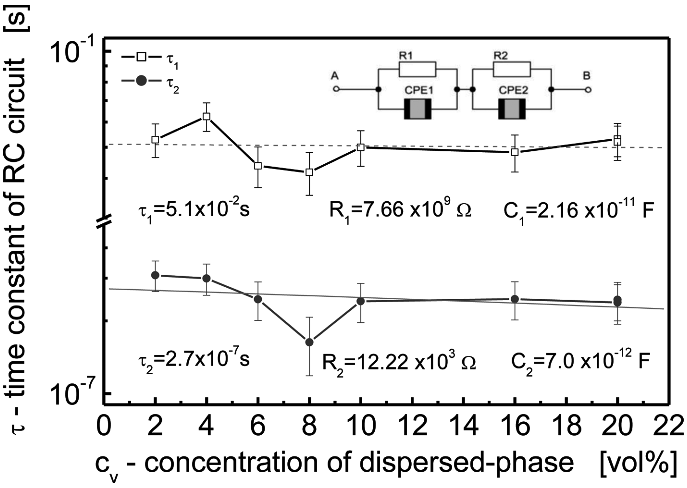

Fig. 7. Dependence of time constants τ_1 and τ_2 of equivalent electric circuit (R1CPE1)(R2CPE2) on concentration of dispersed phase (c_V) for $BiNbO_4$//PVDF composites. Error bars were calculated as standard deviation from the calculated values of τ_1 and τ_2

According to the strategy of impedance spectroscopy analysis [13, 14] the assignment of arcs to the bulk and grain boundary regions is based on the magnitude of the associated capacitance, assuming a brickwork model for the ceramic microstructure. The resolution of arcs depends on the difference between their associated time constants. In many cases [13] the higher frequency arc (bulk) has an associated capacitance of a few pF. In the present case of $BiNbO_4$//PVDF composites the parameters of parallel RC elements are as follows: $R_1 = 7.66\times10^9\Omega$, $C_1 = 2.16\times10^{-11}$ F and $R_2 = 12.22\times10^3$ Ω, $C_2 = 7.0\times10^{-12}$ F.

Calculations showed that the parallel combination of (R1CPE1) appeared as a low frequency "spike" on Cole-Cole plot ($\varepsilon'' - \varepsilon'$ plane) and its contribution to the total impedance of composites in the measuring frequency range at room temperature is dominant. Based on the high value of R1 component the (R1CPE1) circuit can be ascribed to PVDF matrix. On the other hand, starting from frequency about $\nu \approx 10$ kHz the contribution of the second parallel circuit (R2CPE2) became significant. Its contribution was an increase in dielectric losses (Fig. 6*b*).

On the base of dielectric measurements of $BiNbO_4$//PVDF composites as well as taking into consideration results of dielectric measurements of the components of the composites i.e. PVDF [7] and $BiNbO_4$ [15] one can conclude that the dependences of both real and imaginary parts of dielectric permittivity on frequency are mainly governed by poly(vinylidene fluoride) polymer. Although the shapes of the dependences in question for pure PVDF and $BiNbO_4$//PVDF were similar, $BiNbO_4$ dispersed-phase caused an increase in a value of the dielectric loss factor as compared to pure PVDF from $\varepsilon'' = (0.01\text{-}0.10)$ to (0.10-1.0) within the measured frequency range. Real part of dielectric permittivity for $BiNbO_4$//PVDF was also increased from $\varepsilon' \approx 1$ typical for non-modified α-PVDF to $\varepsilon' \approx 10$ in the present research. In this connection it is worth noting that real part of dielectric permittivity for $BiNbO_4$ ceramics changed its value within the range $\varepsilon' \approx 50\text{-}20$ for frequency of the measuring field ν =100Hz-1MHz [15].

4. Conclusion

In the present study we have fabricated the ceramic-polymer composites of 0-3 connectivity using bismuth niobate $BiNbO_4$ fine powder and PVDF polymer powder by hot pressing method. It was found that $BiNbO_4$ powder exhibited orthorhombic symmetry with *Pnna* (52) space group and following lattice parameters a =5.6796(2) Å, b =11.7114(4) Å and c =4.9819(2) Å. PVDF polymer powder was mainly α-phase. Also the three strongest PVDF peaks positions on X-ray diffraction patterns did not changed with the increase in $BiNbO_4$ content. It was found that the ceramic loading decreased intensity of PVDF phase X-ray reflections. For concentration of the dispersed $BiNbO_4$ phase $c_V \geqslant 10$vol% the major phase visible by X-ray diffraction method was α-$BiNbO_4$ phase.

Dependences of the real and imaginary parts of dielectric permittivity for $BiNbO_4$//PVDF composites with 0-3 connectivity on frequency of the measuring field showed that for concentration of (ceramic powder) c_V =2-20vol% dielectric properties are determined in general by the polymer phase: dielectric losses were smaller as compared to $BiNbO_4$ ceramics and dielectric permittivity was higher as compared to PVDF polymer. It was found that dielectric permittivity and dielectric losses of $BiNbO_4$//PVDF composites at room temperature depend on concentration of dispersed phase and reach a local minimum for c_V =10vol% of $BiNbO_4$ powder. It can be ascribed to the distribution of the ceramic particles in a PVDF matrix and possibly to percolation threshold.

The equivalent circuit method made it possible to resolve two relaxation processes namely, a low frequency one connected to the PVDF polymer matrix: $R_1 = 7.66\times10^9\Omega$, $C_1 = 2.16\times10^{-11}$ F and a high frequency one connected to the dispersed $BiNbO_4$ ceramic phase: $R_2 = 12.22\times10^3\Omega$, $C_2 = 7.0\times10^{-12}$ F (bulk region).

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