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COMPOSITES THEORY AND PRACTICE

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CERAMIC-POLYMER COMPOSITES FOR MICROWAVE APPLICATIONS

Ceramic-polymer composites with ferroelectric properties provide significant opportunities in the design and manufacture of modern electronic materials whose functional characteristics are constantly being improved. Barium titanate (BT) and barium strontium titanate (BST) are known and widely used materials in electronics. The paper presents the results of research on a receiving ceramic-polymer composite with an as low as possible permittivity and loss tangent. As a ceramic fraction barium-strontium titanate (BST) with various dopants (Fe_2O_3, Ni_2O_3, La_2O_3, SnO_2 and Y_2O_3) were tested and as an organic one - water dispersions of styrene-acrylic polymers. The influence of BST doped with metal oxides on the sintering process was observed. X-ray diffraction patterns were made for sintered powders while the Vickers hardness, relative density and volume shrinkage of sintered pellets were studied. The zeta potential as a function of pH for pure BST and doped with Ni_2O_3 were measured. BST doped with Ni_2O_3 had the best relative density and this powder was used for further research. For the aqueous tape casting method four water dispersions of polymers with different concentrations and structures as binders were tested. For these polymers heat flow as a function of temperature by differential scanning calorimetry (DSC) and the glass transition temperature were measured. Additionally, the concentration of water dispersion of the polymers was tested by the gravimetric method. For the obtained ceramic - polymer composites, the relative permittivity and loss tangent were measured at a 9 GHz frequency.

Keywords: **ceramic-polymer composites, barium strontium titanate, aqueous tape casting, microwave frequency**

KOMPOZYTY CERAMICZNO-POLIMEROWE DO ZASTOSOWAŃ MIKROFALOWYCH

Kompozyty ceramiczno-polimerowe o właściwościach ferroelektrycznych dają znaczne możliwości przy projektowaniu i wytwarzaniu nowoczesnych materiałów elektronicznych o nowych i wciąż udoskonalanych cechach użytkowych. Znanym od lat i powszechnie stosowanym materiałem w elektronice jest tytanian baru (BT) oraz tytanian barowo-strontowy (BST). Domieszkowanie BST tlenkami metali powoduje zmianę parametrów elektrycznych (np. przenikalności dielektrycznej, tangensa kąta strat) oraz fizycznych (twardości, zagęszczenia). W niniejszej pracy badano wpływ domieszek (Fe_2O_3, Ni_2O_3, La_2O_3, SnO_2 i Y_2O_3) na proces spiekania BST w zakresie 1200÷1400°C. Przeprowadzono analizę rentgenograficzną otrzymanych proszków, a także zbadano mikrotwardość Vickersa, względne zagęszczenie spieków oraz ich skurczliwość objętościową. Wykonano pomiary potencjału zeta w funkcji pH dla czystego BST oraz domieszkowanego 2 i 8% mol Ni_2O_3. Na podstawie otrzymanych wyników wybrano proszek o najlepszym zagęszczeniu (BST + 5% mol Ni_2O_3) i dobrano spoiwo polimerowe oraz upłynniacz, aby otrzymać gęstwę odpowiednią do odlania folii metodą *aqueous tape casting*. Istotne było dobranie polimerów obniżających lub niewpływających znacząco na wartość względnej przenikalności dielektrycznej, ponieważ po procesie formowania folia nie była już spiekana. Badano wodne dyspersje polimerów styrenowo-akrylowych o różnych stężeniach, które wyznaczono metodą wagową. Wykonano pomiary zmiany strumienia ciepła w funkcji temperatury metodą skaningowej kalorymetrii różnicowej (DSC) i na podstawie tej zależności wyznaczono temperaturę zeszklenia analizowanych polimerów. Uzyskane kompozyty ceramiczno-polimerowe o różnych zawartościach proszku ceramicznego (60 i 55%) oraz różnych ilościach domieszek (2, 5 i 8% mol) poddano badaniom względnej przenikalności dielektrycznej oraz tangensa kąta strat przy częstotliwości 9 GHz.

Słowa kluczowe: **kompozyty ceramiczno-polimerowe, tytanian barowo-strontowy, aqueous tape casting, częstotliwości mikrofalowe**

INTRODUCTION

Recognition of the potential usefulness of ferroelectric materials in tunable high-frequency devices dates back over 40 years [1]. However, due to various reasons related to both device electronics and materials technology, it is only in the past decade that intensive development efforts have been made in this direction [2]. $BaTiO_3$ (BT) is a typical ferroelectric material and a base material for multilayer ceramics capacitors. The large permittivity in BT ceramics is attributed to ionic polarization and dipole polarizations related to the ferroelectric domain [3]. The solid solution of $Ba_xSr_{1-x}TiO_3$ (BST) is a ferroelectric material which offers the opportunity to be used in microwave techniques. It is connected with the characteristic dependence of permittivity in a constant or very slowly changing field strength [4]. Depending on the barium concentration, this material exhibits a permittivity maxima within the temperature range 0÷390 K, similar to that of single crystals and ceramics. A high enough value of dielectric permittivity can be obtained by choosing a proper barium concentration and the trend "the higher the barium concentration, the higher the microwave loss" is clearly seen [2].

Ceramic-polymer composites form a potential material group suitable for producing demanding and functional packages that combine the electrical properties of a ceramic and the mechanical strength and flexibility, chemical stability, and processing possibilities of polymers. The prepared flexible composites may be applied in radio communication and security purposes, for example for the detection of dangerous objects and substances. Flexible electronic materials may be also used as devices adjustable to different substrates and shapes, for example as elements for clothes or for application directly on the body. In addition, some polymers have a very low loss tangent, and especially thermoplastic polymers have good thermal properties matching the processing requirements of multilayer RF (radio frequency) structures. The relative permittivity and loss tangent of BST-polymer composites depend on the ceramic loading of the composites. The relative permittivity of the composites gradually increases as a function of the BST fraction (for example: for 30 wt. % of BST relative permittivity was 4.82, for 50 wt. % - 6.96 and for 70 wt. % - 13.46). The dielectric loss behavior of the composites was the same, however, the loss tangent remained quite low (<0.003 at 1 GHz), which is a promising characteristic for multilayer devices in the high frequency range [5, 6].

The applied polymers should have improved adhesion to a metal surface to facilitate connection with metal electrodes. Tunable components based on ferroelectric thin films could play a major role in creating a new type of the low-cost devices. Nowadays, most of phase shifters contain a microwave semiconductor module. Using ferroelectric films enables integration of the phase shifters with the microwave circuits on one substrate, thus substantially reducing the size, mass and cost of the antennas.

The advantages of ferroelectric based phase shifters are: fast speed of tuning, lower cost, high power handling capability and high radiation resistance in comparison to both the semiconductor and ferrite devices. For more phased arrays, the key phase shifter requirements are: low insertion losses and low cost.

This research concerns the development and application of flexible ferroelectric ceramic-polymer composites, stable in temperature range (–40 +60°C), for tunable microwaves and mm-wave electronic devices like tunable antennas, tunable filters and phase shifters. The main purpose was to study the effect of the composition on the high frequency properties of BST - styrene-acrylic polymer composite. BST with the molar formula $Ba_{0.65}Sr_{0.35}TiO_3$ was doped with various metal oxides (Fe_2O_3, Ni_2O_3, La_2O_3, SnO_2 and Y_2O_3). As an organic part of the composite four water dispersions of styrene - acrylic polymers with different concentrations were tested [7].

EXPERIMENTAL PROCEDURE

For the experiments the following materials were used: $BaCO_3$ (CHEMPUR, Poland), $SrCO_3$ (CHEMPUR, Poland), TiO_2 (ALDRICH), Fe_2O_3 (Johnson Matthey Chemicals Limited), Ni_2O_3 (Fluka - Garantie), La_2O_3 (International Enzymes Limited), SnO_2 (Johnson Matthey Chemicals Limited), Y_2O_3 (ALDRICH). As the organic compounds for aqueous tape casting four different water dispersions of styrene - acrylic polymers as binders and ammonium polyacrylate as a dispersant were tested.

The mol of barium strontium titanate was prepared from 0.65 mol of $BaCO_3$, 0.35 mol of $SrCO_3$ and 1 mol of TiO_2. The appropriate quantities of ceramic powders were mixed in water using a mill and ceramic grinding media for 3 hours. The weight ratio of the ceramic powder, water and grinding media was 1:2.5:2.5. Then the obtained suspension was dried at 80°C to a constant weight.

After drying the ceramic powders were calcined at 1150°C during 3 hours. The dopants (2, 5 or 8 molar % of Fe_2O_3, Ni_2O_3, La_2O_3, SnO_2 and Y_2O_3) were added in two different ways: single-step (dopants added directly before sintering) and double-step (dopants added after calcination). The checked range of sintering temperature was 1200÷1400°C, because from differential thermal analysis, it arose that the synthesis occurs between 1200 and 1470°C. After sintering the ceramic had to be ground.

The Vickers hardness was measured for pellets sintered at 1350°C with a load 0.1 kG. The pH of the isoelectric point for pure BST, doped with 2 and 8 molar % of Ni_2O_3 was determined by zeta potential measurements vs pH (Zetasizer Nano ZS, Malvern Instruments). X-ray diffraction patterns were made for pure and doped BST, and the most interesting results are presented in this paper. The density of BST was tested on a helium pycnometer (AccuPyc II 1340).

The heat flow vs temperature and resulting from this the glass transition temperature for polymers, were tested by differential scanning calorimetry (DSC). The concentration of water dispersion of the polymers was tested by the gravimetric method.

The composite films were made by the aqueous tape casting method. Figure 1 shows a block diagram of receiving thin films by the tape casting method. The permittivity and the loss tangent as a function of frequency at 9 GHz are shown.

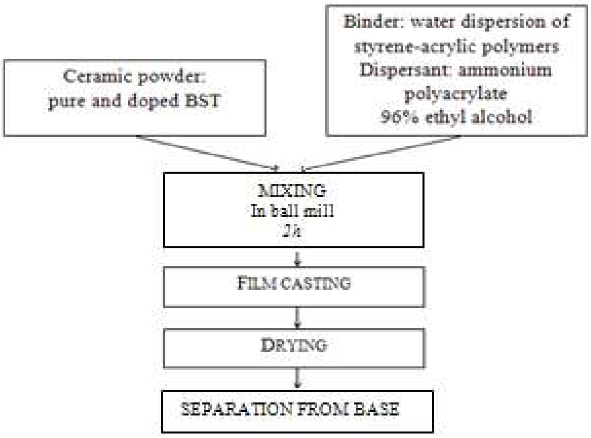

Fig. 1. Block diagram of receiving thin films by tape casting method

Rys. 1. Schemat blokowy otrzymywania cienkich folii metodą tape casting

RESULTS AND DISCUSSION

The pore distribution of BST doped with 5 molar % Ni_2O_3 microstructure is presented in Figure 2. The material is very homogenous, but still shows significant porosity.

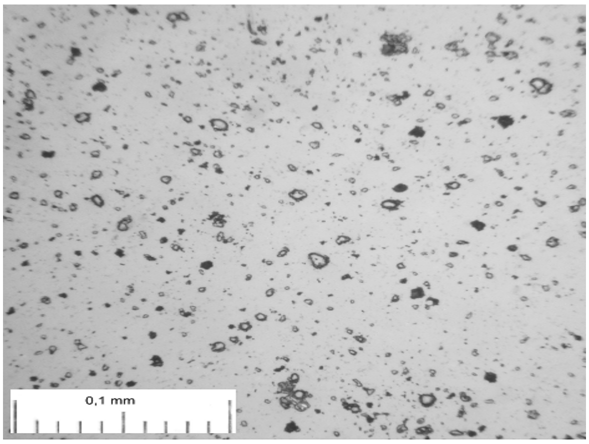

Fig. 2. Microstructure of BST doped with 5 molar % Ni_2O_3

Rys. 2. Mikrostruktura BST domieszkowanego 5% mol Ni_2O_3

Table 1 represents the physical and mechanical properties of pure and doped BST sintered at 1350°C. It is easy to notice that BST + Fe_2O_3 is the hardest material. The densest one is BST + Ni_2O_3. BST doped with La_2O_3 has the worst properties and this sample did not sinter within the checked range of temperature.

Figures 3-5 show the X-ray patterns of pure BST and that doped with 5 molar % of La_2O_3, SnO_2 and Ni_2O_3. Probably, the La^{3+} ions were built into the crystal structure of BST, nevertheless, there is no difference between the pure and doped BST and it is difficult to say where the dopant is located. The Sn^{4+} ions probably were built into the crystal structure in the place of Ti^{4+}. The signal from Ni_2O_3 is visible in the XRD pattern. Probably nothing or not the whole amount of dopant was built into the BST crystal structure.

TABLE 1. **Physical and mechanical properties of sintered pure BST and doped with Fe_2O_3, Ni_2O_3, La_2O_3, SnO_2 and Y_2O_3**

TABELA 1. **Właściwości fizyczne oraz mechaniczne spieków z czystego BSTi domieszkowanego Fe_2O_3, Ni_2O_3, La_2O_3, SnO_2 i Y_2O_3**

		BST + 5 molar % of oxide				
	BST	Fe	Ni	La	Sn	Y
Properties of sintered samples						
Volume shrinkage [%]	45.96	44.73	44.07	10.91	40,31	37.75
deviation [%]	1.82	0.14	1.18	1.53	0.39	0.14
Relative density [%]	88.15	93.98	96.05	52.09	90.95	82.83
deviation [%]	1.51	0.22	0.39	0.38	0.46	0.29
Mechanical properties						
Vickers hardness [GPa]	3.84	9	5.29	0.4	4.75	4.03
deviation [GPa]	0.19	0.95	0.4	0.02	0.67	0.28

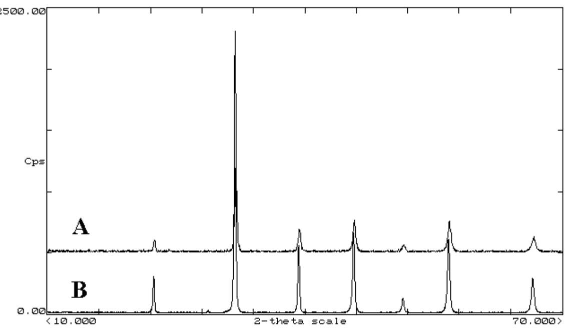

Fig. 3. XRD patterns of BST doped with La_2O_3 (A) and pure BST (B)

Rys. 3. Obrazy dyfrakcyjne BST domieszkowanego La_2O_3 (A) i czystego BST (B)

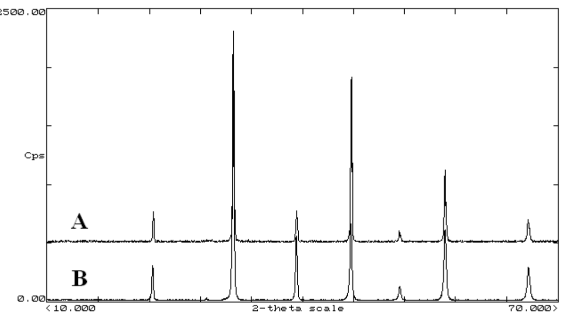

Fig. 4. XRD patterns of BST doped with SnO_2 (A) and pure BST (B)

Rys. 4. Obrazy dyfrakcyjne BST domieszkowanego SnO_2 (A) i czystego BST (B)

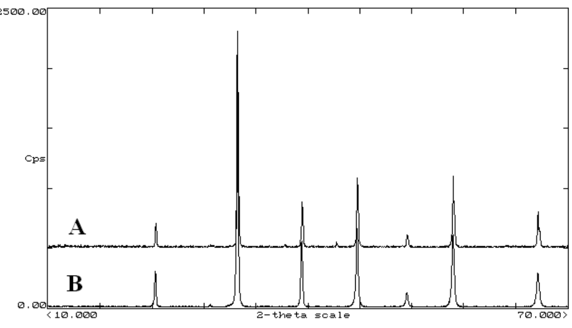

Fig. 5. XRD patterns of BST doped with Ni_2O_3 (A) and pure BST (B)

Rys. 5. Obrazy dyfrakcyjne BST domieszkowanego Ni_2O_3 (A) i czystego BST (B)

The pycnometric density of BST doped with 2 and 8 molar % Ni_2O_3 was as follows: $d_{BST+2\%Ni2O3}$ = 5.6836 ± 0.0046 g/cm^{3}and $d_{BST+8\%Ni2O3}$ = 5.7168 ± 0.0070 g/cm^3.

The zeta potential curves as a function of pH of pure BST and doped with 2 and 8 molar % Ni_2O_3 are presented in Figure 6. The dopants have a small influence on the point of zero charge and the stability areas.

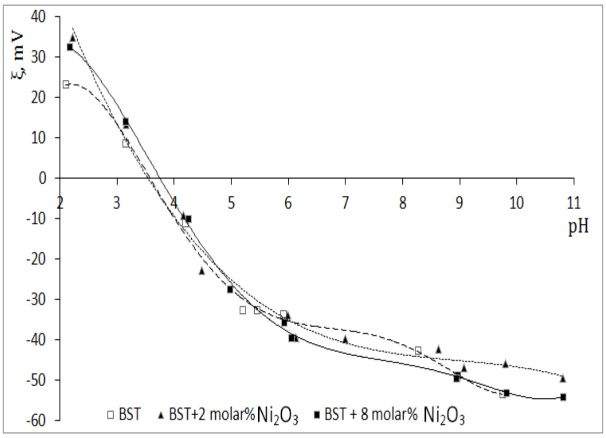

Fig. 6. Zeta potential as a function of pH of BST, BST+2 molar % Ni_2O_3 and BST+8 molar % Ni_2O_3

Rys. 6. Potencjał zeta w funkcji pH proszków BST, BST+2% mol Ni_2O_3 i BST+8% mol Ni_2O_3

The concentration of the analyzed styrene - acrylic polymers were as follows: 35.9, 50.2, 57.7 and 58.2%. The best one as a binder was 57.7%, because the received thin layer containing this polymer had the best flexibility, strength and minimum porosity. The dependence of heat flow as a function of temperature for the best polymer is shown in Figure 7. The glass temperature of the analyzed polymer −3.54°C.

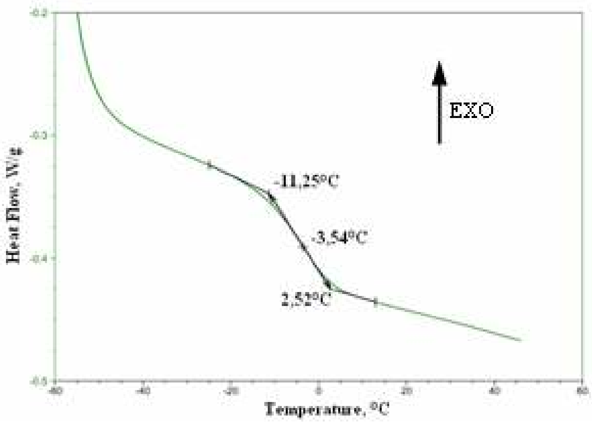

Fig. 7. Heat flow as function of temperature of styrene-acrylic polymer

Rys. 7. Strumień ciepła w funkcji temperatury polimeru styrenowo--akrylowego

The composition of the slurry which gave the composite with the best properties, such as flexibility, strength and lack of porosity was as follows: 62.94 vol.% of ceramic powder (BST doped Ni_2O_3), 35.98 vol.% of binder (water dispersion of styrene - acrylic polymer with concentration 57.7%), 0.25 vol.% of dispersant (10% water solution of ammonium polyacrylate).

The complex permittivity of the composites was measured by means of the split post dielectric resonator (SPDR) method [8, 9]. In this method, the resonant frequency and Q-factor of a sample placed in a SPDR are determined and the complex permittivity of the material is extracted on the basis of an accurate solution of the structure (by means of a radial mode matching method).

The relative permittivity and the loss tangent of the composites at frequency 9 GHz are shown in Table 2. It is clearly see, that the amount of dopants has a smaller impact on the permittivity than the amount of organic part in the composite. Nonetheless, even a small amount of dopant clearly affects the loss tangent.

TABLE 2. **Relative permittivity and loss tangent of composites at 9 GHz frequency**

TABELA 2. **Względna przenikalność dielektryczna i tangens kąta strat kompozytów przy częstotliwości 9 GHz**

BST	Ceramic [vol.%]	Polymer [vol.%]	ε	tgδ ·10^{-2}
pure	60	40	43÷46	4.00÷4.50
+ 2 mol/% Ni_2O_3	60	40	58÷60	2.90÷3.20
+ 8 mol/% Ni_2O_3	60	40	43÷44	2.65÷2.85
+ 5 mol/% Ni_2O_3	60	40	48÷50	2.62÷2.63
+ 5 mol/% Ni_2O_3*	60	40	34÷36	2.32÷2.45
+ 2 mol/% Ni_2O_3	55	45	26÷28	2.30÷2.47
+ 8 mol/% Ni_2O_3	55	45	29÷31	2.46÷2.47
*means one-step doping				

CONCLUSIONS

BST - styrene-acrylic polymer composites were fabricated from BST with various dopants. BST doped with Ni_2O_3 had the best relative density - over 96% theoretical density, and this material's dielectric properties were studied at the 9 GHz frequency. The loss tangent of BST - styrene-acrylic polymer composites depends on the ceramic loading of the composites, while the relative permittivity depends on the amount of polymer in the composites. At higher frequencies, the loss tangent decreases.

Within the tested range of temperature, no effects of sintering in BST doped with La_2O_3 were observed. The Sn^{4+} ions probably were built into the crystal structure in the place of Ti^{4+}. Ni_2O_3 is seen in the XRD pattern and probably none or not the whole amount of dopant was built into the crystal lattice of BST.

Dopants have a small impact on the point of zero charge and the BST stability areas.

As a binder for the tape casting method the best polymer turned out the water dispersion of styrene-acrylic polymer with a concentration of 57.7%, and as a dispersant - the 10% solution of ammonium polyacrylate. What is also needed is an addition of ethyl alcohol. In further research we should investigate other types of polymer dispersions as binders, for instance based on silicon combinations.

The tested composites showed promising high frequency electrical characteristics in addition to the fact, that the films were made by the aqueous tape casting method. This method is environmentally friendly and does not have a negative influence on human health.

Acknowledgements

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