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COMPOSITES THEORY AND PRACTICE

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TUNABLE CERAMIC-POLYMER COMPOSITES FOR ELECTRONIC APPLICATIONS

The ceramic-polymer composites presented in the paper have unusual properties. These materials can operate in a wide range of electromagnetic spectrum and consequently they can be potentially used in imaging techniques, chemical characterization, security systems, quality control and very high data rate communication systems. Microwave applications are widely understood as antennas and radiocommunication devices. Materials used to produce equipment operating at high frequencies, even subterahertz, must be subjected to restrictive verification. The most commonly used materials in radio technology are ferroelectrics. They are characterized by a high value of dielectric permeability. A typical example of ferroelectric material used and widely known is barium strontium titanate (abbr. BST), which is applied in microwave technology. Barium strontium titanate was prepared using solid-state synthesis process. The materials used in the fabrication were ceramic powders: $BaCO_3$, $SrCO_3$ and TiO_2. Thanks to the combination of an elastic polymer and ceramic powder with ferroelectric properties, it is possible to use such a material in devices operating at a very high frequency. The commercial materials used in the research allow one to produce composites by the tape casting method and obtain antennas. Ferroelectric ceramic-polymer tapes based on doped and undoped ceramic powder with different BST stoichiometrics have been prepared. The tunability of samples prepared of pure and doped $Ba_{0.65}Sr_{0.35}TiO_3$, $Ba_{0.58}Sr_{0.42}TiO_3$ and $Ba_{0.51}Sr_{0.49}TiO_3$ was measured. The relationship between the stoichiometry, or doped and undoped powder has been also found. It was observed that a higher ratio of Ba to Sr caused an increase in tunability values. Moreover, the addition of Ni_2O_3 to ceramic powder positively effected the tunability parameter.

Keywords: tunability, ceramic-polymer composites, BST (barium strontium titanate), tape casting

PRZESTRAJALNE KOMPOZYTY CERAMIKA-POLIMER W ZASTOSOWANIACH ELEKTRONICZNYCH

Kompozyty ceramiczno-polimerowe przedstawione w niniejszej pracy charakteryzują się niezwykłymi właściwościami. Materiały te posiadają zdolność pracy w szerokim spektrum elektromagnetycznym, dzięki czemu mogą być wykorzystywane w obrazowaniu materiałów, analizie chemicznej, systemach ochrony, kontroli jakości oraz w telekomunikacji intersatelitarnej. Zastosowania mikrofalowe są szeroko rozumianymi antenami oraz urządzeniami radiokomunikacyjnymi. Materiały wykorzystywane do otrzymywania urządzeń pracujących w wysokich częstotliwościach sub-THz są poddawane restrykcyjnej weryfikacji. Najbardziej powszechnymi materiałami używanymi w technologii radiowej są ferroelektryki. Charakteryzują się one bardzo wysoką wartością przenikalności dielektrycznej. Typowym przykładem materiału ferroelektrycznego jest powszechnie znany tytanian barowo-strontowy (BST). Proszek stosowany do badań syntezowany był w fazie stałej z następujących substratów: $BaCO_3$, $SrCO_3$ i TiO_2. Charakterystyczne właściwości BST powodują, że stał się on kluczowym komponentem ceramicznej masy lejnej, która umożliwia, za pomocą metody tape casting, otrzymanie cienkich i elastycznych folii kompozytowych. Ferroelektryczne ceramiczno-polimerowe folie bazowały na czystych oraz domieszkowanych proszkach BST o różnym stosunku baru do strontu. Pomiary przestrajalności przeprowadzono dla proszków $Ba_{0.65}Sr_{0.35}TiO_3$ i $Ba_{0.58}Sr_{0.42}TiO_3$ z dodatkiem Ni_2O_3 oraz bez dodatku. Zaobserwowano zależność stechiometrii proszków oraz domieszki tlenku niklu na przestrajalność kształtek. Im większa zawartość Ba do Sr, tym wyższe wartości przestrajalności. Z badań wynika również, że pozytywny wpływ na przestrajanie ma dodatek 5% mol Ni_2O_3.

Słowa kluczowe: przestrajalność, kompozyty ceramika-polimer, BST (tytanian barowo-strontowy), tape casting

INTRODUCTION

Composite technology allows one to modify material properties for specified applications. The properties are determined by the choice and amounts of components.

A combination of elastic polymer (which provides high mechanical strength) and ceramic powder with ferroelectric properties allows one to use this type of composite in devices operating at a very high frequency up to sub-terahertz [1].

Ferroelectric materials are the most often used materials in electronic techniques and radio communication. They are characterized by a high value of dielectric permeability [2].

Barium strontium titanate is a typical example of a ferroelectric material, which is applied in microwave technology. The application results from its dielectric permittivity which depends on a constant or nearly constant electric field [3]. Perovskite $Ba_xSr_{1-x}TiO_3$ is a material with a high dielectric constant value (up to 5000), which depends on its purity, grain size, method of preparation and crystallographic direction. Additionally BST is characterized by a low value of dielectric loss, high mechanical strength, negligible effect of aging and good thermal stability [4-6].

The characteristic properties of barium strontium titanate make it a key component of a suspension which enables one to obtain thin films by the tape casting method. The tape casting technique is a well-known process used in the fabrication of very thin sheets of flexible tapes. The obtained ceramic-polymer composites are characterized by suitable thermal stability, durability, flexibility, homogeneous surface, resistance to vibration and are environmentally friendly (Fig. 1). For this reason, these materials are competitive in designing many different tunable devices such as antennas, phase shifters and filters.

Fig. 1. Ferroelectric composite tape
Rys. 1. Ferroelektryczna folia kompozytowa

The intensive research on ferroelectric composites was started over 15 years ago by the team from the Faculty of Chemistry, Warsaw University of Technology and Institute of Radioelectronics. However, the first study on ferroelectric materials in devices operating at high-frequency was conducted over 50 years ago [7, 8].

This work concerns the development and application of tunable ceramic-polymer composites for electronic devices. The most important thing was appropriate selection of the components for the ceramic slurry which enabled the authors to obtain flexible tapes. Samples based on doped and undoped ceramic powder with different BST stoichiometrics. The composite material should characterized by a smooth surface without any defects. It is required for microwave applications and tunability measurements.

EXPERIMENTAL PROCEDURE

Materials

The ceramic powder used in the research was barium strontium titanate of an average particle size from 0.5 to 0.9 μm. In the experiments ceramic powders doped with 5 mol% Ni_2O_3 (> 99.9%, ALDRICH) and undoped were used. The barium strontium titanate was prepared by using a solid-state synthesis process. The synthesized material was fabricated using the following substrates: $BaCO_3$ (> 99.9%, CHEMPUR), $SrCO_3$ (> 99.9%, CHEMPUR) and TiO_2 (> 99.9%, POCH, Poland). The BST powders were synthesized at 1350°C for 2 hours.

Ceramic slurries were prepared by using many components such as ethanol (POCH, Poland) as the solvent, ethylene glycol (CHEMPUR) as the plasticizer, KD1 (UNIQEMA) as the dispersant and aqueous polyurethane-acrylic dispersion DPU-PJ 538 as the binder. The water-thinnable polymeric dispersion was prepared at the Industrial Chemistry Research Institute by Prof. J. Kozakiewicz's team.

The concentration of ceramic powder and other additives in the ceramic slurry are presented in Table 1.

TABLE 1. **Concentration of components in ceramic slurry**
TABELA 1. **Stężenie komponentów w ceramicznej masie lejnej**

Chemical agent	Concentration
Ceramic powder (BST)	55 vol.%
Solvent (ethanol)	45 vol.%
Plasticizer (ethylene glycol)	0.2 wt.% (with respect to the ceramic powder)
Dispersant (KD1)	0.5 wt.% (with respect to the ceramic powder)
Binder (dispersion DPU-PJ 538)	52 wt.% (with respect to the ceramic powder)

An appropriate combination of components and selection of conditions of the tape casting process enable one to obtain tunable, thin and flexible tapes.

Tape-casting procedure

Samples were obtained in several steps by means of the tape casting process. Firstly, the components of the ceramic slurry were put into a zirconia container. The suspensions were ball milled for 1 hour at a mixing speed of 200 rpm at room temperature. The preparation of a ceramic slip having suitable parameters is essential to make high-quality tapes. After mixing, thin samples were prepared by the tape casting technique. The slurry passed beneath the knife's edge (commonly referred to the doctor blade) which controlled the thickness of the tapes (Fig. 2). The thickness of the composite tapes was about 100-300 μm. The materials were dried slowly at room temperature for 24-48 hours. After that process, the tapes were removed from the carrying tape and cut for electrical measurement. The block diagram of composite tape preparation is presented in Figure 3.

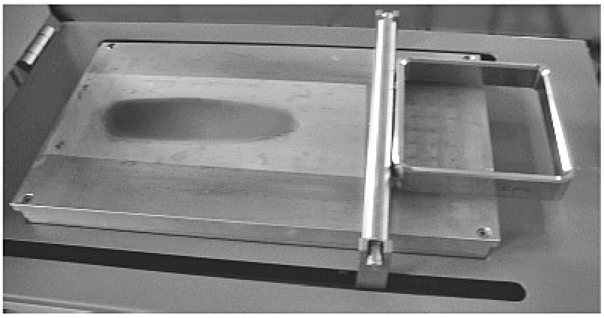

Fig. 2. Preparation of thin composite tapes by tape casting technique

Rys. 2. Otrzymywanie cienkich kompozytowych folii przy użyciu metody tape casting

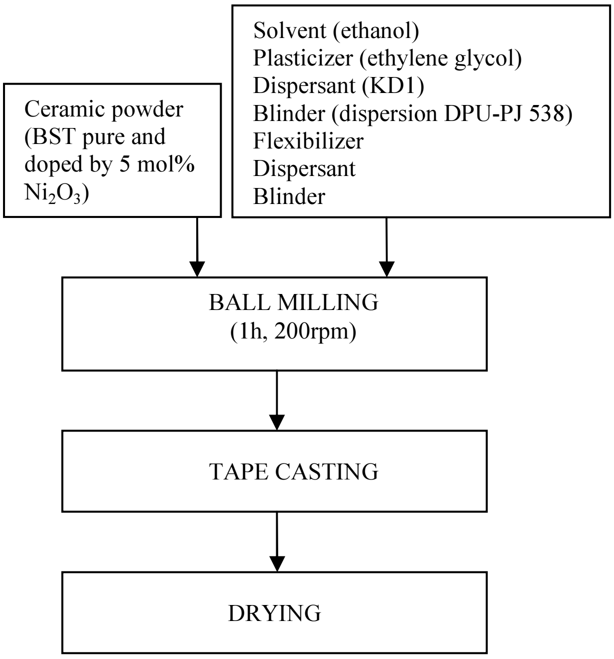

Fig. 3. Block diagram of composite tape preparation

Rys. 3. Schemat blokowy przygotowania folii kompozytowych

Thanks to the combination of the polymer and ceramic powder it was possible to obtain a composite with significant properties which are suitable for microwave applications. The composite tapes should be characterized by good mechanical strength, flexibility, negligible porosity and a smooth surface.

Measurement setup

Tunability is the main parameter which was measured by the team from the Institute of Radioelectronics using a Vector Network Analyzer. The scheme of the measurement setup is presented in Figure 4. For the analysis, the microstrip transmission line mode was employed.

A copper path was laid on the tapes and finally a high DC voltage was applied to polarize the samples. In this method, a very important step is appropriate preparation of the composite tape before the analysis. It is necessary to ensure good contact of the substrate with the tapes, without an air gap between these two surfaces, because it causes large measurement errors [9, 10].

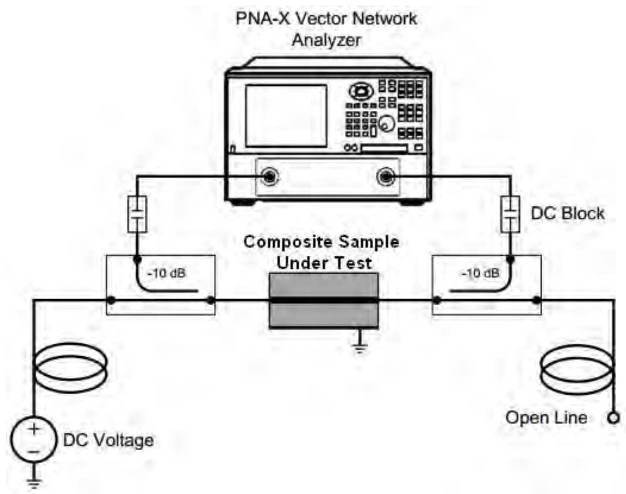

Fig. 4. Scheme of measurement setup [9, 10]

Rys. 4. Schemat układu pomiarowego [9, 10]

Measurements were performed in the frequency range from 100 MHz to 20.1 GHz and for several values of biasing voltage. The tunability parameter as a function of electric field ($\eta(E)$)was calculated:

$$\eta(E)=\frac{\varepsilon_r(E)-\varepsilon_r(0)}{\varepsilon_r(0)}\times 100\% \tag{1}$$

where $\varepsilon_r(E), \varepsilon_r(0)$ - the relative permittivity of the ferroelectric ceramic-polymer composite with and without an applied electric field

The measurements were performed at room temperature.

The full fabrication method is the subject of patent application No P 410683.

RESULTS AND DISCUSSION

Tapes fabricated by using pure and doped BST with different ratios of barium to strontium were measured. Samples were prepared with the same solid content (55 vol.%). Figure 5 presents the results of tunability measurements of selected samples based on three different ratios of barium to strontium ($Ba_{0.65}Sr_{0.35}TiO_3$, $Ba_{0.58}Sr_{0.42}TiO_3$ and $Ba_{0.51}Sr_{0.49}TiO_3$) for 10 GHz.

As can be seen, tunability depends on the amount of barium in the ceramic powder. The higher ratio of barium to strontium, the higher tunability effect.

The favorable composition $Ba_{0.65}Sr_{0.35}TiO_3$ was characterized by approximately 8% tunability.

The tunability measurements of BST pure and doped with 5 mol% Ni_2O_3 are presented in Figure 6. The samples based on the doped ceramic powder had an influence on the tunability value. The addition of nickel oxide led to an increase in the measured values. According to the results obtained, a significant growth in the tunability value (from 8 to 25% for samples based on ceramic powder $Ba_{0.65}Sr_{0.35}TiO_3$) was observed.

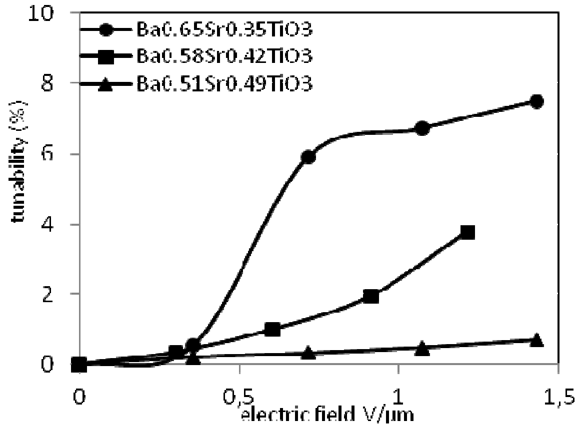

Fig. 5. Tunability of samples based on BST with different ratio of Ba to Sr

Rys. 5. Pomiary przestrajalności dla kształtek na bazie BST o różnym stosunku Ba do Sr.

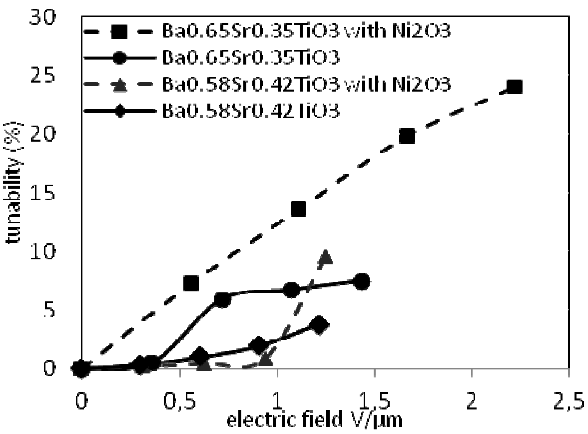

Fig. 6. Influence of nickel oxide on tunability value

Rys. 6. Wpływ tlenku niklu na wartość przestrajalności

The next studies are going to be conducted on the fabrication of multilayer structures with the use of prepared tapes. Electronic devices should operate in a wide range of electromagnetic spectrum and thus they can be potentially used in microwave applications.

CONCLUSIONS

Ferroelectric ceramic-polymer composites are a very promising group of materials which can be used in microwave applications. They are able to change their dielectric permittivity. Moreover, they can be used to develop tunable devices operating in a wide range of frequencies up to sub-THz.

The optimized composition of the slurry enabled the authors to obtain thin and flexible tapes based on barium strontium titanate and an aqueous polymeric dispersion. The sample made of doped $Ba_{0.65}Sr_{0.35}TiO_3$ had the best microwave properties with tenability above 25%. Furthermore, the addition of 5 mol% Ni_2O_3 caused an increase in the tunability value. Barium strontium titanate (BST) thin tape is one of the most promising candidates for applications in electronically controlled microwave tunable devices.

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