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 56 2011 Issue 4
DOI: 10.2478/v10172-011-0117-6

K. KOGUT*, B. ZBOROMIRSKA-WNUKIEWICZ*, K. KASPRZYK*

CERAMIC NANOMATERIALS BASED ON THE BARIUM AND TITANIUM COMPOUNDS, PREPARED BY THE SOL – GEL METHOD, FOR ELECROTECHNICAL APPLICATIONS

NANOMATERIAŁY CERAMICZNE NA BAZIE ZWIĄZKÓW TYTANU I BARU PRZYGOTOWANE ZA POMOCĄ METODY ZOL – ŻEL DO ZASTOSOWAŃ W ELEKTROTECHNICE

This paper describes the sol – gel method barium and titanium compounds materials obtaining, which their physicochemical parameters could be competitive with the materials obtained by classic methods. Additionally dielectric thin layers was obtained with the use of spin and dip coaters. Based on selected precursor elements which form appropriate crystal net, the capacitance construction was created. Dielectric in this contraction was a barium titanate with high electrical permittivity and small grain size. The optimal dry, calcinations and sintering temperature of the dielectric with base was determined. On that capacitor the microscopic analysis with the use of scanning electron microscope (SEM) was carried out. The thickness of the dielectric layer and electrical parameters use by impedance analyzer Solatron SI 1260 was carried out. The capacitance, dielectric loss and electrical permittivity was carried out, cooperative influence of the frequency and temperature on the measurements was determined. The best results had a samples sintered in the 1000°C. The electrical permittivity for measurements in few Hertz for the samples with the base of nickel and $BaTiO_3$ layer coated by spin and dip coaters, in the room temperature and measurements for few Hertz, amount to 4700. The electrical capacity for low frequency was about $3{,}2 \cdot 10^{-8}$F.

Keywords: Barium titanate, dip coating, electric permittivity, sol – gel method, spin coating

W pracy przedstawiono metodę zol – żel otrzymywania materiałów na bazie związków tytanu i baru, których właściwości fizykochemiczne mogą być konkurencyjne dla materiałów uzyskiwanych metodami klasycznymi. Dodatkowo wykorzystując urządzenia typu spin i dip coater uzyskano cienkie warstwy dielektryczne. Na podstawie wytypowanych prekursorów pierwiastków tworzących odpowiednią sieć krystaliczną, wykonano układ pojemnościowy, w którym dielektryk stanowił tytanian baru o wysokiej wartości przenikalności elektrycznej i niewielkich rozmiarach ziaren. Wyznaczono optymalną temperaturę suszenia, kalcynacji i wypalania dielektryku wraz z podłożem.

Na przygotowanym elemencie stanowiącym rodzaj kondensatora wykonano analizę mikroskopową za pomocą elektronowego mikroskopu skaningowego oraz przeprowadzono pomiary grubości nałożonych warstw jak i pomiary właściwości elektrycznych wykorzystując analizator impedancji Solatron SI 1260. Wyznaczono pojemność elektryczną, współczynnik strat dielektrycznych, przenikalność elektryczną materiału, określając jednocześnie wpływ częstotliwości i temperatury na wyniki pomiaru.

Stwierdzono, że najlepszymi wynikami charakteryzowały się próbki wypalane w temperaturze 1000 ^{o}C. Wartość przenikalności przy częstotliwości pojedynczych herców dla próbek o podłożu ze stali kwasoodpornej z cienką warstwą BaTiO3 wypalanych w 1000°C, przy temperaturze pomiarowej 40-50°C, wynosiła ok. 300 zaś w podwyższonych temperaturach pomiaru przenikalność osiągała wartość rzędu 14000. Dla próbek gdzie podłoże stanowił nikiel a warstwa BaTiO3 nakładana była za pomocą metod spin coatingu i powolnego zanurzania, już w temperaturze pokojowej przy pojedynczych hercach zmierzona wartość przenikalności elektrycznej osiągała wartości rzędu 4700. Pojemność elektryczna przy pomiarze dla niskich częstotliwości osiągała wartości rzędu $3{,}2 \cdot 10^{-8}$F.

1. Introduction

Dielectrics are very important group of electrotechnical materials. These materials can be applicant in many discipline, for example as a ceramic surge arresters, insulators, or separating materials in capacitors [1].

The materials based on titanium and barium compounds received in the past strong attention in electrical engineering. These materials are often prepared via sol – gel method [2].

Based on the literature and our experience sol – gel method was applied to obtained barium titanate

* ELECTROTECHNICAL INSTITUTE DIVISION OF ELECTROTECHNOLOGY AND MATERIALS SCIENCE IN WROCŁAW, 50-369 WROCŁAW, M. SKŁODOWSKIEJ-CURIE 53/61, POLAND

with the molar ratio of Ba:Ti 0.9:1.0. As a precursors: tetrabutyl- $Ti[O(CH_2)_3CH_3]_4$ and hydroxide hydrated barium- $Ba(OH)_2 \bullet 8H_2O$ were used.

$C = \frac{\varepsilon\varepsilon_0 s}{d}[F]$This paper is devoted to the synthesis of new ceramic materials with barium titanate and their electrical and structural characterizations. The main aim of work is obtain materials with large value of electric permittivity and use the fundamental equation (1) on the electric capacity [3].

$$C = \frac{\varepsilon\varepsilon_0 s}{d}[F] \tag{1}$$

where:

ε_0 – electric permittivity in vacuum 8,854287817 · 10-12 F/m,

ε – electric permittivity of the material,

s – surface area of the conductor,

d – separation distance between the plates.

To the construction of the capacitor appropriate medium should be chosen being into considering melting temperature and stress arising from the difference in coefficient of thermal expansion. Two types of substrate such as steel acid and nickel was used. However, based on the literature experience and the thermal properties as the electrode nickel was chosen. On nickel electrode thin layers of sol was coated. For this purpose spin ad dip coaters was used. The thickness of the obtained layer was about 50 μm.

The process of drying, calcination and sintering was carried out. Next on the dielectric, nickel electrodes was coated by cavity magnetron. These samples were investigated by electron scanning microscopy (SEM) where the size of the grains was defined. The electrical measurements of investigated materials including: measurements of volume resisitivity, measurements of the electric permittivity, capacitance and the coefficient of dielectric loss, both as a function of frequency and temperature.

2. Materials based on barium and titanium compounds

Ferroelectric materials based on titanium and barium compounds due to the high value of the electric permittivity, which under certain conditions (temperature Curie about 120°C) can be up even at the level of several thousand, are widely applicable, for example in the construction of capacitors [4, 5]. Barium titanate is used from the 1950's of the 20th century. But the chemical method of sol-gel has been applied since the eighties of the 20th century.

The production uses various precursors, which are the source of the main elements of the compound, which form a crystalline net [6]. It was examined many aspects that need to be taken into account during production, which may significantly affect the physico-chemical properties of the resulting material [7]. One of the key are: mixing times, grinding, calcination and sintering temperature and the size of the grains, as well as the stoichiometric ratio of elements and the homogeneity of the gel [8, 9].

Generally, these materials can be classified into perovskite groups. The name of the structure comes from the mineral called perovskite, having the chemical formula $CaTiO_3$. Shows the structure of a cube $CaTiO_3$ (Fig. 1a), but actually it is a structure of orthorhombic. All of a group of perovskite show the construction with the general formula ABO_3[10].

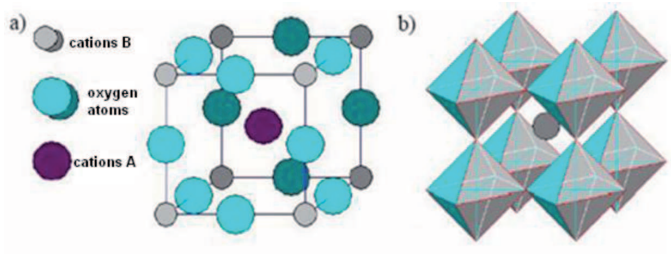


Fig. 1. Perovskite structure [10]

3. Sol-gel method

Nanomaterials can be obtained, for example by the sol-gel method (Fig. 2), which consists of a slow dehydrate of previously prepared alcoholate sol of metal hydroxide and, leading to a change of sol in gel [11, 12].

This method is used in the following reaction of hydrolysis of alcoholates:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH,$$

where: M – the atom of the metal,

n – the valency,

R – alkyne groupe,

and its products are hydroxide and alcohol. Precipitate hydroxide of metal, in order to make it into a colloidal solution (sol), add quantity of acid. Research has shown that the speed of the peptization depends on the temperature. Dewatering of sol by method of evaporation leads to its passage in the gel. The next step is the roasting of the gel at temperature of 400-850°C, which gives the powders, for example oxides. This step determines the shape and particle size and capacity of powder sintering (Fig. 2).

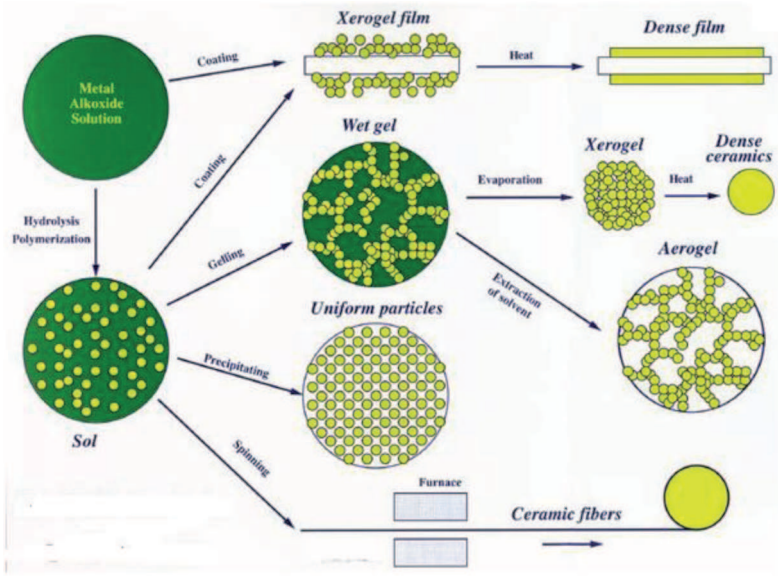


Fig. 2. Sol-gel method [13]

Method of sol-gel enable to produce fibers using draw directly from the solution. Materials obtained by this method are characterized by a high uniformity and purity, and the process of sintering can be implemented at a much lower temperatures than conventional method for the production of powders [14, 15].

The reduction in the size of the crystallites to the nanometer fundamentally affects the properties of dielectric ceramic materials. For ferroelectrics -offset Curie temperature towards lower temperatures with the reduction of particle size, over the easier distribution of additives ions derived from source solution, than in the case of the traditional process of doped powders [16].

4. The coating processes – spin and dip coating

In recent years increasingly to impose thin layers using sol-gel method. This process consists in the imposition of sol to the ground and then carry out the process of gelling, and in subsequent stages, drying and burn gel. If sol imposes in an appropriate manner to the ground, the product obtained after the whole process of drying, calcination and burning will result in a thin layer. In most cases, to cover the ground (usually with nickel or tantalum owing to the high melting temperature and the good properties of conductive) colloid layer solution uses methods of spin and dip coating. Method of spin coating imposition of thin layers is used relatively recently.

The typical process of spin coating involves the deposition of the solution in the middle of the ground and then rotate at high speed, typically of 2000-3000 rpm (Fig. 3).

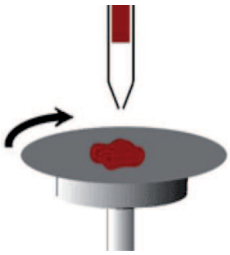


Fig. 3. Spin coating process [17]

Very important is the smoothness of the surface of the ground as well as the viscosity and density of sol and accuracy of deployment of substratum. Centripetal acceleration causes the spread of the thin film of sol to the edge of the ground, as result lead to outside the sol from the ground, which in effect redistributes cover thin film across the ground.

Properties of the resultant layers are dependent on many factors: viscosity of sol, drying temperature, surface tension, acceleration and speed ground together from a tax levied gel, the duration of the sample, etc.

One of the most important factors is the repeatability of the process. Subtle differences in parameters that describe the process of spin coating can result in drastically affect the parameters and properties obtained the thin layer.

Sol, characterized by a high viscosity, and the ground with a greater surface area require higher speeds during the process of imposition.

Generally that higher speed and longer time turnover leads to receive thinner layers [17].

Figure 4 shows the dip process, which can describe the coating using the 5 steps such as: 1) immersion, 2) start the submarine surfaced, 3) the imposition of a

shell, 4) evaporation and 5) drying [18, 19, 20]. Surface coating method of "dip coating" consists in immersing a substrate in the solution, and than go to a specific speed. For the smoothness of surface influence the temperature and humidity of the air. This technique is suitable mainly for the coating of the flat surface and often leads to cover both the surface simultaneously. Any unilateral requires additional treatment. The technique produces a uniform coating, however, is very sensitive to small local change in the temperature of the ground.

There is a relationship that slowly withdrawn is the medium that is creates a thinner film. The technique allows to obtain optically homogeneous coating thickness 20 nm – 50 mm by changing the speed of retrieving and viscosity of the solution. Frequently used speed to impose a 1-15 cm/min [21].

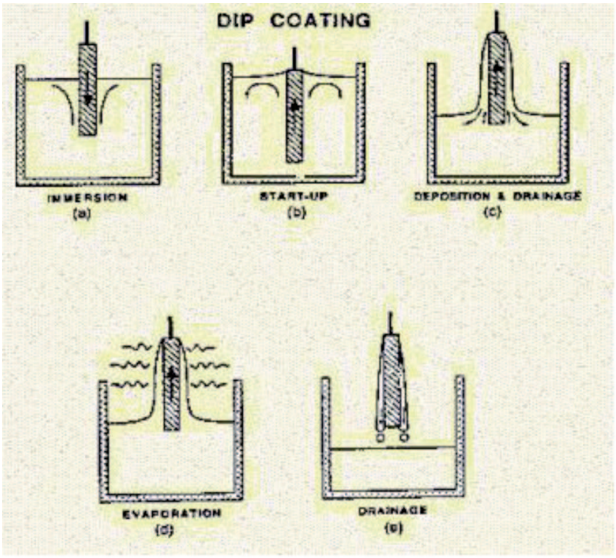


Fig. 4. Dip coating method [18]

5. Multilayer capacitors

Capacitor is comprised with electrodes separated by dielectric. Using the property to the capacity to ability of a body to hold an electrical charge, it is appliance can store electricity energy. The capacity of the flat capacitor depends on its dimensions.

Of the bases of the electrotechnical know that connecting capacitors can increase or reduce capacity based system.

To obtain the maximum capacity of the replacement system parallel connections is used. However in such system the voltage can be replenished.

In the case of the simultaneous connections entire voltage system accumulates on each from capacitors, while in the case of the serial, the voltage at each capacitor is equal to $\frac{U}{n}$, where n is the number of identical capacitors. This is very important in view of the permissible voltage capacitors work.

Application of parallel connection of layers dielectrics covered electrodes used in the construction of power multilayer capacitors (Fig. 5), whose capacity is equal to:

$$C = \frac{\varepsilon_0 \varepsilon_r (n-1)s}{d} \tag{2}$$

where: C is the capacity of the multilayer capacitor, ε_0 is the permittivity 8.85 · 10-12 F/m, ε_r is the permittivity of the environment, s – surface area of electrodes, d is the thickness of the dielectric layer (the distance between the electrodes), n is the number of electrodes.

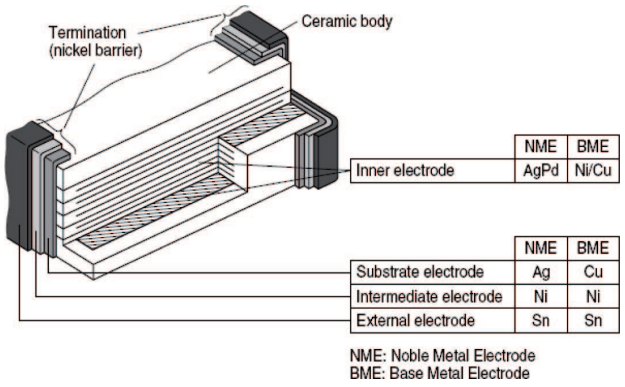
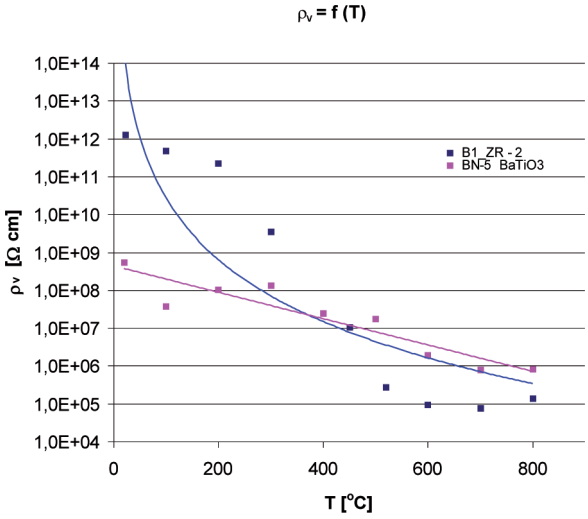


Fig. 5. Multilayer capacitor (MLC) in the parallel layer connection [22]

6. Results

On the basis of the measurement of particle size and parameters as a dielectric in capacitive construction $BaTiO_3$ was chosen. That material undoped ZrO was obtained by sol-gel method. Barium titanate was sintered at different temperatures in the range 800°C to 1200°C. The smallest size of particles was obtained by sintering at 1000°C and was about 150-200 nm. $BaTiO_3$ doped with ZrO was sintered in temperatures of 1200°C and 1400°C. The particle size of $BaTiO_3$ doped with ZrO was about 100 nm. This behavior suggested the possibility to obtain thinner layers in the case of undoped $BaTiO_3$. However $BaTiO_3$ doped with ZrO has much lower permittivity and higher value of the volume resistivity (Fig. 6) presented as a function of temperature than undoped $BaTiO_3$. This relationship was strongly nonlinear for $BaTiO_3$ doped with ZrO in comparison with undoped $BaTiO_3$.

Nickel was applied as a substrate for the electrodes of a flat capacitor construction. It was also considered other metals but taking into account the temperature coefficients of each metal from the point of view of the stresses which may occur during the process of heat treatment material felt that seemed appropriate, as the metallic substrate, nickel. Its melting point is 1453°C



B1 - sample doped ZrO
BN-5 –$BaTiO_3$ sample not doped

Fig. 6. Relationship of volume resistivity from the temperature for $BaTiO_3$ and $BaTiO_3$ doped ZrO

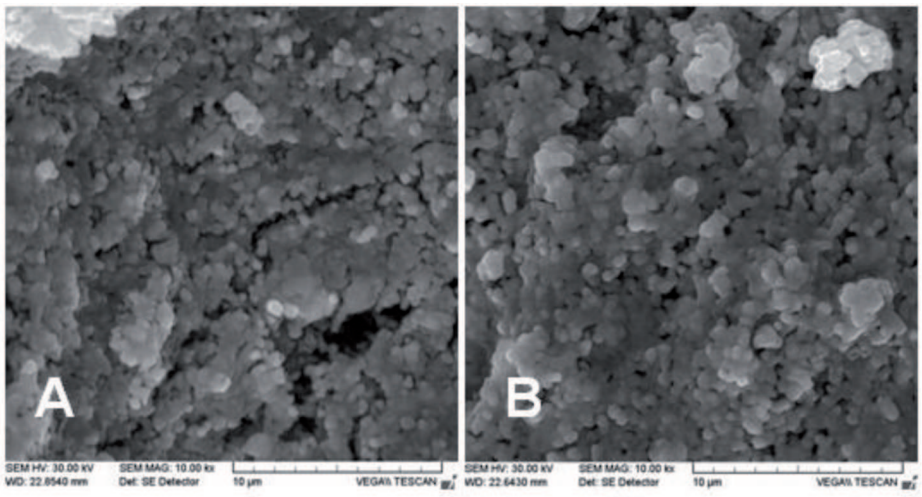


Fig. 7. SEM images of $BaTiO_3$ imposed on the ground of nickel: A – using the spin coating, B – using dip coating method

and the coefficient of thermal expansion is at the level of 15.9 10^{-6} 1/(C). The value of the coefficient of thermal expansion for $BaTiO_3$ is 10.6×10^{-6} 1/K [23, 24]. The ratio of the coefficients of thermal expansion of metal and dielectric in this case is about 1.5.

Using spin and dip coater the sol layer on the ground were imposed. Then have them processes, drying, calcination and sintering. Electron scanning microscope (SEM) was applied to describe the size grains of dielectric both imposed by spin coating (Fig. 7 A) and dip coating (Fig. 7 B).

The size of the smallest grains $BaTiO_3$ sintered at 1000°C was about 200-250 nm. For electrical measurements samples with nickel electrodes coated by cavity magnetron were investigated. The value of the electric permittivity, electrical capacity and dielectric loss factor was estimated. Impedance analyzer – Solatron SI 1260 was used to investigated dielectric properties of the materials. The real and imaginary coefficients of the electric permittivity was estimated by used the formulas 3 and 4:

$$(\varepsilon')^2 = \frac{d^2 \cdot (Z'')^2}{\omega^2 s^2 Z^4} \rightarrow \varepsilon' = \frac{d \cdot Z''}{\omega s Z^2} \tag{3}$$

$$\varepsilon'' = \frac{d \cdot Z'}{\omega s Z^2} \tag{4}$$

Figure 8 shows the results of the measurements of the electric permittivity of $BaTiO_3$ imposed by spin coating method, sintered at the temperature 1000°C with nickel plate in function of frequency in different temperatures.

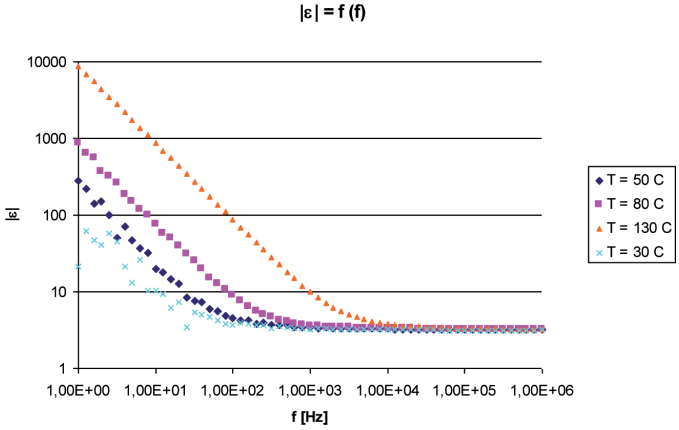


Fig. 8. Relationship of the electric permittivity of $BaTiO_3$ imposed on the nickel plate and sintered at 1000°C as a function of frequency

Figure 9 shows the dependence of electric permittivity as a function of temperature for the same sample. The frequency of measurement was a single Hertz.

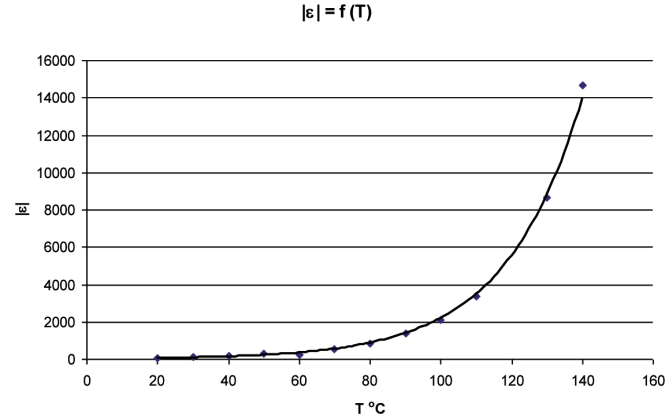


Fig. 9. Relationship of the electric permittivity from the temperature at a frequency measuring individual Hertz

The figure 9 shown that the Curie temperature is within 140°C. On the basis of own experiences and literature it was found that the addition of the ZrO moves toward the lower values Curie temperatures. However, as described previously in the ZrO addition caused a reduction in the value of the electric permittivity of material representing a significant problem in achieving the intended purpose. Therefore, it was decided that $BaTiO_3$, without ZrO will be used as the dielectric.

The value of coefficient of dielectric loss was relatively large for measurements at low frequencies (Fig. 10). However, the frequency of 50 Hz was interesting because of its applications and value of tgδ was found about 0.09. Together with the increase in the frequency of the coefficient value of the dielectric loss is increasing. Moreover, along with increase measurement temperature from 30 to 130°C increase of tgδ was observed (Fig. 10).

Figure 11 shows the value of the capacitance as a function of frequency for the $BaTiO_3$ with the nickel electrodes, sintered at temperatures of 850 and 1000°C. Measurements carried out at a temperature of 40°C.

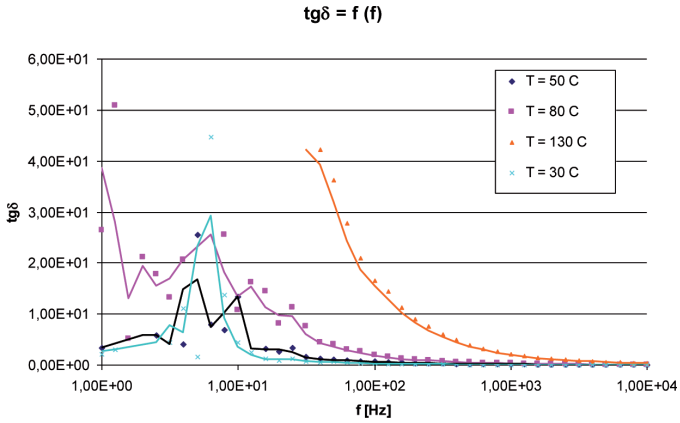


Fig. 10. The dependency of dielectric loss factor as a function of frequency for a variety of temperature measurement

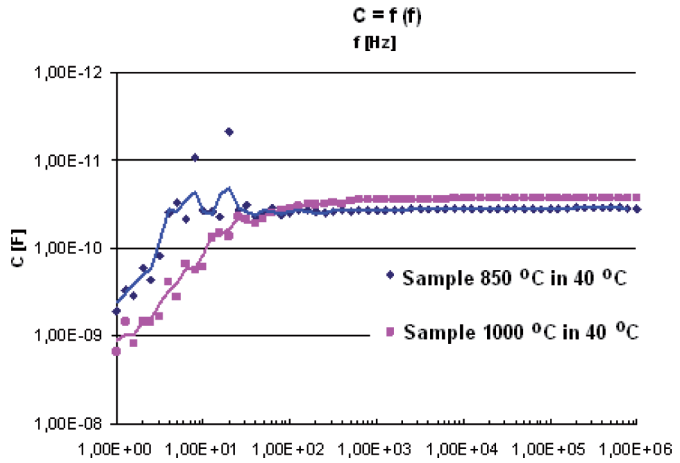


Fig. 11. The relationship of capacitance as a function of frequency for $BaTiO_3$ imposed on the nickel plate by using of spin coating method and sintered at 1000°C

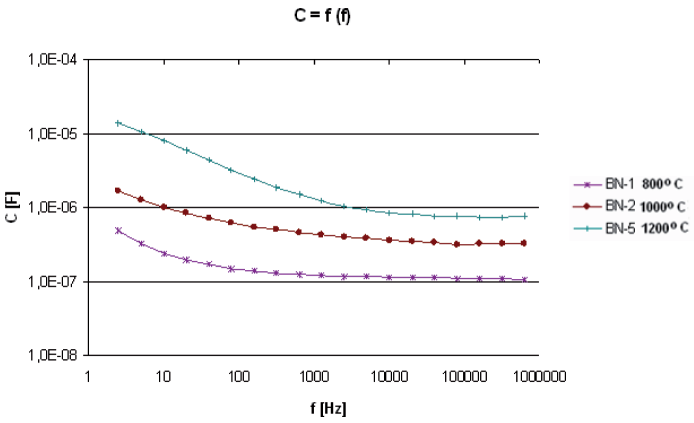


Fig. 12. The relationship of $BaTiO_3$ sintered in three different temperatures as a function of frequency

Where such measurements have the only material without nickel plate sintered in three different temperatures (BN-1 800°C, BN-2 to 1000°C and 1200°C-5 BN)

the capacitance values were higher then for materials with Ni plate (Fig. 12).

Spin and dip coating methods were used to prepare capacitors and their electric capacity was compared. There were not determine differences in the results of the measurement (Fig. 13).

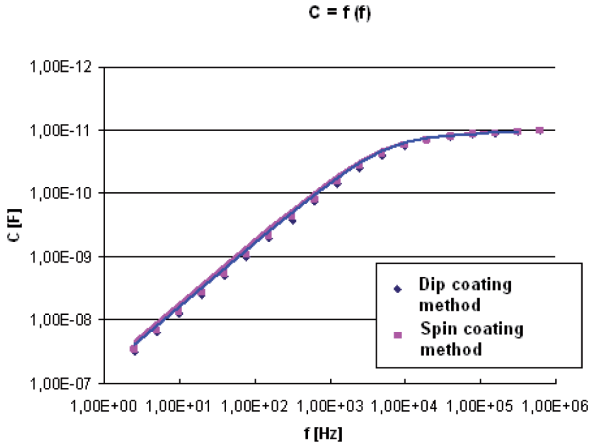


Fig. 13. The relationship of capacitance as a function of frequency for both methods impose thin dielectric layers

7. Conclusions

The following conclusions can be drawn from the present work:

- Ceramic nanomaterials based on barium and titanium compounds, prepared by sol-gel method were obtained.
- Spin and dip coating methods enable dielectric $BaTiO_3$ thin layers forming.
- Using fundamental formulas, materials obtained by sol-gel method, the electrical parameters, as electric permittivity and capacitance, could be increased.
- Sol-gel method and spin and dip coating processes are used to multilayer capacitors creation.
- Electric permittivity of $BaTiO_3$ was about 11 000 for single Hertz, and about 4000 for frequency 50 Hz.
- The capacitance system with the nickel plate, nickel electrodes and nanoceramic $BaTiO_3$ as the dielectric exhibit a high electric permittivity and capacitance ε about 4700. For high measurement temperature, the electric permittivity was about 14 000. Capacitance for frequency of single Hertz was about $3.2 \cdot 10^{-8}$F.
- Such results could be a premise to engage those materials, methods and capacitors construction for the multilayer capacitors production.

REFERENCES

[1] K. Kogut, B. Mazurek, K. Kasprzyk, B. Zboromirska-Wnukiewicz, Factors affecting the mechanism of flashover in metal oxide surge arrester, Archives of Metallurgy and Materials **54**, 4, 1013-1020 (2009).

[2] K. Kogut, K. Kasprzyk, B. Zboromirska-Wnukiewicz, The materials with high electrical permittivity available to the capacitive constructions, PhD Workshop, Lublin 2010, „Prace Instytutu Elektrotechniki", Paper 248, 161-174 (2010).

[3] K. Kogut, B. Zboromirska-Wnukiewicz, K. Kasprzyk, T. Ruziewicz, K. Gryzła, R. Kłoś, The method of nanolayers preparing with high electrical permittivity, based on the barium and titanium compounds, with the use of the sol-gel method, for electrotechnical application. Phase 2., Electrotechnical Institute Technical Documentation No 500-9320-26, 2010.

[4] R. n. Viswanath, S. Ramasamy, Preparation and ferroelectric phase transition studies of nanocrystalline BaTiO3, Nanostructured Materials **8**, 2, 155-162 (1997).

[5] Salvatore A. Bruno, Donald K. Swanson, High performance Multilayer Capacitor Dielectrics from Chemically Prepared Powders, Journal American Ceramics Society **76**[5], 1233-1241 (1993).

[6] U. Hasenkox, S. Hoffmann, R. Waser, Influence of precursor chemistry on the formation of MTiO3 (M=Ba, Sr) ceramics thin films, Journal of Sol-Gel Science and Technology **12**, 67-79 (1998).

[7] R. Thomas, D.C. Dube, M.N. Kamalasanan, N. Deepak Kumar, Electrical Properties of Sol-Gel Processed Amorphous BaTiO3 Thin Films, Journal of Sol-Gel Science and Technology **16**, 101-107 (1999).

[8] K. Gomi, K. Tanaka, H. Kamiya, Effect of Miting Conditio on Sol-Gel Synthesis of Bariom Titante ultrafine Particles, KONA No. 22, 177-185 (2004).

[9] R. Balachandran, H.K. Yow, M. Jayachandran, Wan Yusmawati Wan Yusof, V. Saaminathan, Particle Size Analysis of Barium Titanate Powder by Slow – Rate Sol-Gel Process Route, ICSE 2006 Proc., Kuala Lumpur, Malaysia, 406-409 (2006).

[10] Hsiao-Lin, Wang, Structure and dielectric properties of Perovskite – Barium Titanate (BaTiO3), Submitted in Partial Fulfillment of Course Requirement for MatE 115, Fall 2002, San Jose State University.

[11] O. Harizanov, A. Harizanova, T. Ivanova, Formation and characterization of sol-gel barium titanate, Material Science and Engineering B **106**, 191-195 (2004).

[12] T. Makino, M. Arimura, K. Fujiyoshi, Y. Yamasita, M. Kuwabara, Crystallinity of barium titanate nanoparticles synthesized by sol-gel method, Key Engineering Materials **350**, 31-34 (2007).

[13] http://sariyusriati.wordpress.com/2008/10/21/sol-gel-technology/

[14] M. Jurczyk, J. Jakubowicz, Ceramic Nanomaterials, Publisher – University of Technology Poznań, Poznań 2004.

[15] M. Veith, S. Mathur, N. Lecerf, V. Huch, T. Decker et al., Sol-Gel Synthesis of Nano-Scaled BaTiO3 and BaTi0,5Zr0,5O3 Oxides via Single – Source Alkoxide Precursors and Semi – Alkoxide Routes, Journal of Sol-Gel Science and Technology **15**, 145-158 (2000).

[16] Woo-Seok Cho, Structural evolution and characterization of BaTiO3 nanoparticles synthesized from polymeric precursor, J. Phys. Chem. Solids **59**, 5, 659-666 (1998).

[17] Spin Coating Process Theory Description – http://www.clean.cise.columbia.edu/process/spintheory.pdf

[18] http://www.science.unitn.it/~gcsmfo/facilities/dip-coating.htm

[19] H.R.C.S. Andrade, N.D.S. Mohallem, M.M. Viana, L.M. Seara, Barium titanate thin films prepared by dip-coating process, 11th International Conference on Advanced Materials Rio de Janeiro Brazil, 20 – 25 September, ICAM 2009.

[20] J. Rosenberger, R. Nass, H. Schmidt, Crystallization behavior of barium titanate thin films, Eurogel, 91', Elsevier Science Publishers BV **92**, 343-349.

[21] http://webcache.googleusercontent.com/search?q=cache:bgckEuOd7coJ:www.oknoserwis.pl/art,82,,szklo,czytelnia.html+defekty+przy+dip+coating&cd=4&hl=pl&ct=clnk&gl=pl

[22] Epcos – General Technical Information.

[23] J.M.J. den Toonder, C.W. Rademaker, Ching-Li Hu, Residual Stresses in Multilayer Ceramic Capacitors: Measurement and Computation, Journal of Electronic Packaging, Transaction f the ASME **125**, 503-511 December 2003.

[24] J.R.G. Keyston, J.D. Macpherson, E.W. Guptill, Coefficient of thermal expansion of barium titanate, The review of scientific instruments **30**, 4, 246-248 (1959).

Received: 20 April 2011.