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Influence of electric field DC-component on AC-response of ferroelectric powder

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ABSTRACT

Purpose: of this work was to establish whether ac-response of freely stocked micro-granular ferroelectric matter on fringe measuring electric field depends on constant component presence VDC (or DC-Bias).

Design/methodology/approach: used involves measurements of effective dielectric permittivity (and other effective dielectric quantities) by means of interdigit dielectrometry. Fringe measuring electric field was applied to $BaTiO_3$ micro-powder by interdigit comb sensor (ICS) Netzsch of Ms25 type. ICS was driven by measuring generator with sinusoidal voltage: v(t)= VDC+VACsin(ωt), within frequency range 20Hz-100kHz and for DC-Bias values ranging as VDC=(0-20)V.

Findings: The interdigit dielectrometry was applied to measure complex dielectric permittivity, complex dielectric modulus and others dielectric functions of ferroelectric $BaTiO_3$ powder. The influence of constant component of electric stimulus was investigated in the frequency range 100 kHz to 20 Hz. It was established that in the low frequency range constant component of electric field enhances effective dielectric permittivity, and changes two weak relaxation processes occurring in the ferroelectric micro-granular net. It turned out that effective dielectric complex modulus of this net is most sensitive quantity for application of constant component of electric stimulus.

Research limitations/implications: The density solution effect is a source of small effective dielectric permittivity of micro-granular ferroelectric powder (ε'). ε' values are being enhanced by presence of non zero VDC value. The same effect was established for effective energy loss coefficient (ε"). The two relaxational processes connected with VDC≠0 seems to be a key feature of freely stocked ferroelectric matter.

Originality/value: of this work relays on the fact, that this is a first report of the VDC influence on effective dielectric properties of ferroelectric micro-granular matter. It is opening the way to a new approach in modelling of effective dielectric properties of granular matter in nature and powders technology.

Keywords: Ferroelectric $BaTiO_3$ powder; Effective dielectric permittivity; Interdigit dielectrometry

MATERIALS

1. Introduction

Investigations of basic physical properties of powders are stimulating a knowledge development about new materials structures – properties correlations. They enables designing of new practical applications of these materials [1-3].

The interdigit dielectrometry applies flat, comb electrode sensor (form of flat capacitor) and was originally developed for polymers curing process monitoring [4-6]. Now, it is widely applied for dielectric monitoring of many different processes [7-9]. Interdigit planar electrodes are used as sensors in dielectrometry, as chemical sensors, humidity sensors, surface transducers of acoustic waves and many others. There are many

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applications in electrochemistry (electrochemical impedance measurements) [10] and in biology and medicine [11] (sensors of specific biochemical and biophysical effects, detection and monitoring of cells and bio-macromolecules specific reactions and so on). The key feature of planar capacitive electrode is a possibility of easy exposition of small amount of investigated material to light, gases, introduction of micro-amount of chemical reagent for chemical or physical reaction initiation which can be dielectrically detected and monitored. Capacitive interdigital sensors are commercially available with electrodes made of chromium, gold, platinum and with different sizes to be chosen for specific purposes. Simultaneously, the physics of granular or micro-granular matter are subjects of rapid development [12, 13]. The collection of material granules accessible in the macro scale, forms a kind of physical heterogeneous, three dimensional net and its dielectric properties models are subjects of many investigations. The dielectric and electric response of granular matter to DC and AC electric fields stimulus have very important practical meaning because of huge amount of such materials production, transportation and applications in many branches of technology. This kind of physical systems are also present widely in nature. In this work we applied interdigit dielectrometry to $BaTiO_3$ powder in order to establish how the constant component presence in the electric field applied to ferroelectric powder, modifies its effective electric and dielectric response. In our experiment, the scale of observation was determined by active surface of comb sensor (12mm x 10 mm) and the penetration range of electric field (stimulus) which was of the order of 25 µm. It equals the distance between comb electrodes as well as the metallic electrodes width. Taking into account the average micro granules diameter (~0.5µm) and considering the excluded volume of micro-granules packing one can estimate the scale of our dielectric measurements as characterized by the approximate number of ferroelectric granules of about 1500. Thus it means that dielectric functions were measured as effective ones, collected on such micro granules population.

2. Experimental

The $BaTiO_3$ powder with average diameter about 0.5µm, (Inframat Advence Materials LLC, USA) and core density 5.85 g/cm^3 was washed by acetone and methanol and dried in the room temperature. It was kept in the 296K and 29%RH for three days in order to establish its surface properties. The powder layer (about 1mm thick) was placed on the Ms25 (Netzsch) comb sensor within measuring chamber made of plastic or brass. Temperature inside the chamber was 296K and relative humidity (RH) ~ 29%. The temperature was measured by PT100 flat sensor and RE15 Lumel (Poland) microprocesor termoregulator with Lumel-Regulacja program. The RH was stabilized by glycerol – water solution. The RH value was monitored by Oregon Scientific Meter (USA). The all dielectric functions (ε', ε'', M', M'', σ', σ'', Φ) were measured by means of Agilent 4284A precise RLC meter coupled with PC by WinDeta (Novocontrol) program. The constant parameters of the measuring program were adjusted in such a way that $\varepsilon'(\omega)$ function equals 1.0 within the range of frequency 100kHz to 20Hz. Constant component of electric stimulus (DC Bias) were set to V_{DC} = {0V, 2V, 4V, 6V, 8V, 10V, 20V}. The V_{DC} value and polarity were kept constant during the frequency scan. Measurement for each frequency was repeated 10 times and average value was stored in the memory. Each frequency scan lasted about 3 minute and sample was relaxed for about 10 minutes before next scan with new V_{DC} value. The amplitude of AC stimulus component was kept at 10V for all measurements.

3. Results and discussion

The effective dielectric permittivity ($\varepsilon'(\omega, V_{DC})$) dependence for V_{DC} = (0V, 2V, 4V) shows the inflection point at about 1kHz. It vanishes step by step along the V_{DC} increase. The dielectric permittivity increases monotonically from 2.18; (20Hz, 0V=V_{DC}) to about 3.4; (20Hz, 20V=V_{DC}). These increases are of nonlinear character against the V_{DC} values. The effective values of ε' seems to be too small as compared to bulk ferroelectric one as well as those ones connected with water vapors adsorption on others powders. The effective energy loss coefficient ($\varepsilon''(\omega, V_{DC})$) for V_{DC} = (0V, 2V, 4V) changes from ~$4.16\cdot10^{-2}$ (100kHz) to ~2 (20Hz). In double log representation, the conductivity is covering probably two weak relaxation processes, one with visible maximum localization at ~1kHz. The increase of V_{DC} value up to 6V and higher, makes $\varepsilon''=\varepsilon''(\omega, V_{DC})$ run approximately linear but closer inspection shows a subtle deviations from the linear character. The ε' dependence on V_{DC} for f = (100 kHz, 1 kHz, 20 Hz) is shown in the Fig.1.

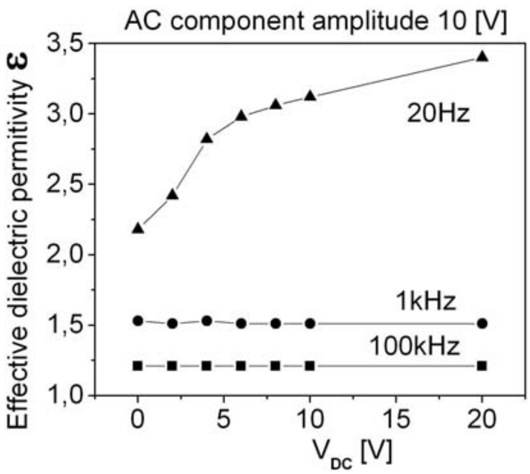

Fig. 1. The real part of effective dielectric permittivity (ε') dependence on constant component values of electric stimulus (V_{DC}) for three selected frequencies. Powder sample of $BaTiO_3$ on Ms25 µm comb sensor

For low frequencies is of nonlinear character. The influence of V_{DC} presence is visible beneath ~500Hz. The imaginary part of effective electric permittivity (ε'') dependence on constant component of electric stimulus (V_{DC}) for 3 selected frequencies is demonstrated in the Fig.2. The influence of V_{DC} presence is not as strong as in the former case but again the nonlinearity occurs. Generally, the changes of measured dielectric functions, induced by V_{DC} application are taking place below characteristic values of AC component frequency for all measured dielectric functions. (The amplitude of AC component was kept at constant level 10V). The Table 1 summarizes the threshold values of frequency for all measured dielectric quantities.

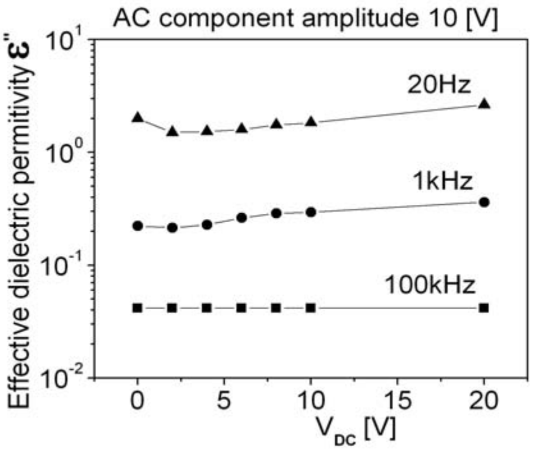

Fig. 2. The imaginary part of effective dielectric permittivity (ε") dependence on constant component values of electric stimulus (V_{DC}) for three selected frequencies. Powder sample of $BaTiO_3$ on Ms25 µm comb sensor

Table 1.
The threshold values of frequency for sensibility of dielectric functions of $BaTiO_3$ powder change, induced by V_{DC} presence in generator signal. The AC component amplitude equals 10V

The dielectric function of $BaTiO_3$ powder	Symbol of function	Threshold frequency for $\frac{dF}{dV_{DC}} \neq 0$
Effective dielectric permittivity	ε'	f ≤ 100 kHz
Effective dielectric loss coefficient	ε"	f ≤ 5 kHz
Dielectric modulus- real part	M'	f ≤ 1 kHz
Dielectric modulus- imaginary part	M"	f ≤ 20 kHz
AC conductivity- real part	σ'	f ≤ 20 kHz
AC conductivity- imaginary part	σ"	f ≤ 60 kHz
Phase angle	Φ	f ≤ 10 kHz

The subtle changes visible on the ε'(ω, V_{DC}) and ε"(ω, V_{DC}) can be identified easy in the M'(ω, V_{DC}) and on M"(ω, V_{DC}) – complex dielectric modulus runs. The two processes are here well separated. The character of these processes are presented in Fig.3 and in Fig. 4.

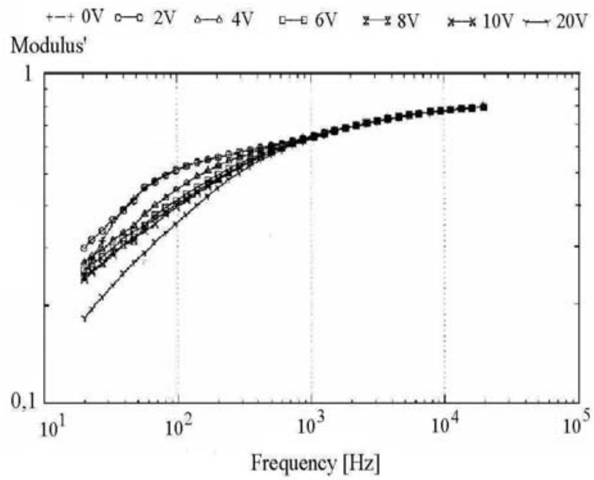

Fig. 3. The real part of effective dielectric modulus (M') dependence on frequency for 7 constant component values of electric stimulus (V_{DC}). Powder sample of $BaTiO_3$ on Ms25 µm comb sensor. The AC component amplitude equals 10V

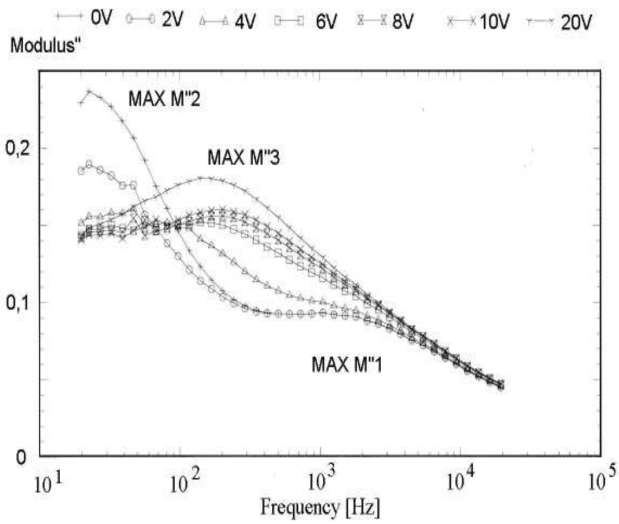

Fig. 4. The imaginary part of effective dielectric modulus (M") dependence on frequency for 7 constant component values of electric stimulus (V_{DC}). Powder sample of $BaTiO_3$ on Ms25 µm comb sensor. The AC component amplitude equals 10V

The measured M'(ω, V_{DC}) functions have two inflection points for V_{DC} values down to ~6V. At V_{DC}~6V only one is being left. The M"(ω, V_{DC}) functions (Fig.4), exhibits two weak relaxation processes (M"1 and M"2). The first one gets MAX.M"1 for about 1kHz and second one more intensive, gets MAX.M"2 at ~25Hz. The increase of V_{DC} values above ~4V damps down process Max.M"2 and elevates that at about 200Hz, assigned as MAX.M"3 in the Fig.4. For $V_{DC} \geq 6V$ both processes M"2 and M"1 superimpose and one broad MAX.M"3 is been observed at ~200Hz.

4. Conclusions

The values of effective real part of dielectric permittivity (ε'), are surprisingly small and equals 1.05 at high frequencies, where they are independent on V_{DC} presence, and about 2,2 at 20Hz (V_{DC} = 0V). The V_{DC} presence elevates effective ε' from 2.2 up to ~3.6 and at low frequencies this dependence is of nonlinear character. The small values of ε' can be interpreted in terms of inter micro granules compensation effect. Following described in the literature [14] view, that ferroelectricity exists even in case of nano-sized grains one can postulate that the compensation effect originates from spatially limited process of “had to tail” configuration of micro grains effective dipole moments creating almost close spatial polygons. The second reason of low effective ε' values can be identified (in our measurements) as the density solution effect. It is connected with much lower effective density of micro-granular set as compared to bulk (core) density of ferroelectric $BaTiO_3$ determined by producer as 5.85 g/cm^3. The two step of ε' increase should be considered (Fig.1). The first rapid one up to ~4V = V_{DC} and the second one, slower up rising taking place from ~4V and up to 20V. The origin of this dependence will be a subject of detailed investigation. It is connected with low frequency behavior so one can postulate that it can originate from possible micro movements and connected with changes of piezo-charges at the sticking of micro-regions between grains. Another aspect to be taken into consideration is the fact of two ferroelectric phases coexistences at 296K in the core of $BaTiO_3$ grains. There is no clarity whether both these phases can be present in one core grain. This question together with the possibility of water molecules adsorption on the outer shell of ferroelectric grains can be also taken into consideration as the origin of weak relaxation processes demonstrated in Fig.3 and Fig.4. The effective polarizability increase under constant component of electric field at low frequencies is an intriguing problem to be investigated in the nearest future [15].

References

[1] R. Nowosielski, R. Babilas, J. Wrona, Microstructure and magnetic properties of commercial barium ferrite powders, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 307-310.

[2] R. Nowosielski, R. Babilas, G. Dercz, L. Pająk, J. Wrona, Barium ferrite powders prepared by milling and annealing, Journal of Achievements in Materials and Manufacturing Engineering 22 (2007) 45-48.

[3] A. Buchacz, Influence of piezoelectric on characteristics of vibrating mechatronical system, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 229-232.

[4] N.F. Shepard, S.L. Garverick, D.R. Day, S.D. Senturia, Microdielectrometry: a new method for in situ cure monitoring, Proceedings of the 26th SAMPLE Symposium, Los Angeles, CA, 1981, 65-76.

[5] S.D. Senturia, N.F. Shepard Jr, H.L. Lee, D.R. Day, In-situ measurement of the properties of curing systems with micro-dielectrometry, Journal of Adhesion 15 (1982) 69-90.

[6] S.D. Senturia, N.F. Shepard Jr, Dielectric analysis of thermoset cure, Advance Polymer Science 80 (1986) 1-49.

[7] A.V. Mamishev, A.R. Takahashi, Y. Du, B.C. Lasientre, M. Zahn, Parameter estimation in dielectrometry measurements, Journal of Electrostatics 56 (2002) 465-492.

[8] A.V. Mamishev, K. Sundara-Rajan, F. Yang, Y. Du, M. Zahn, Interdigital sensors and transducers, Proceedings of the IEEE, 92/ 5, 2004, 808-845.

[9] K. Sundara-Rajan, L. Byrd, A.V. Mamishev, Moisture content estimation in paper pulp using fringing field impedance spectroscopy, IEEE Sensors Journal 13 (2004) 378-383.

[10] Wah On Ho, S. Krause, C.I. Mc Neil, I.A. Pritchard at all, Elecrochemical sensor for measurement of urea and creatinine in serum based on ac impedance measurement of enzyme-catalysed polymer transformation, Analytical Chemistry 71 (1999) 1940-1946.

[11] C. Berggren, B. Bjarnason, G. Johansson, Capacitive biosensors, Electroanalysis 13 (2001) 173-180.

[12] R. Hilfer, J. Widjajakusuma, B. Biswal, Macroscopic dielectric constant for microstructures of sedimentary rocks, Granular Matter 2, Springer-Verlag, 2000, 137-141.

[13] R. Hilfer, Geometric and dielectric characterization of porous media, Pysical Review B (1991) 44-60.

[14] E. Evdem, R. Boetthcher et al., Ferroelectrics 316 (2005) 43.

[15] F. Starzyk, W. Bąk, Application of interdigit dielectrometry to $BaTiO_3$ powder – influence of stimulus constant component on effective dielectric and electric properties, Proceedings of the XVII Czech-Polish Seminar: Structural and ferroelectric phase transitions, Znojmo, 2006, 89.