NONLINEAR PROPERTIES OF BARIUM TITANATE CERAMICS

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Abstract: The materials based on barium titanate have nonlinear dependence of polarization on the intensity of the electrical field. The properties of those materials are used when different automation elements such as primary converters, phase regulators for low and high frequencies, sensors, modulators etc. are derived. Ceramics based on barium titanate ($BaTiO_3$) alloyed with H_3BO_3 and Bi_2O_3 have been derived and researched. The influence of the temperature of sintering on the values of the dielectric permittivity on the structural properties has been determined. The influence of the quantity of the added material on the temperature dependencies and the non-linear properties of the ceramics have been analyzed. Both legation additives decrease the sintering temperature. However, the values of the dielectric permittivity decrease while the non-linear properties of the doped barium titanate ($BaTiO_3$) improve. The coefficient of non-linearity reaches its maximum for the H_3BO_3 composites, synthesized at temperature of 1100 ^oC.

Keywords: barium titanate, non-linear properties, doped additives

1. INTRODUCTION

Advances in modern automation systems require a search for new functional materials, including nonlinear dielectrics whose properties are influenced by an external electric field. Those materials have found application in dynamic RAM, tuneable microwave devices, such as tuneable oscillators, phase shifters, reactors with a large tuneable capacitance range and low dielectric loss, transducers and sensors [1-3], thermistors [4], and multilayer ceramic capacitors [5].

Barium titanate ($BaTiO_3$) is a perovskite-type ceramics material, exhibiting very good properties like low dielectric losses, high values of the dielectric permittivity and high electromechanical coupling coefficients [1].

Lead-free piezoelectric barium titanate and its solid composites are in high demand due to the requirement to find a replacement for lead zirconate titanate (PZT) ceramics. These ceramic materials have high volatility and toxicity, which contaminate the environment [3].

The electrical properties of ferroelectric materials can be modified by doping in or- der to meet the requirements for some applications. The dopants (additions) like NiO, ZrO and Nb_2O_5 influence the grain size and phase transition temperature of the Barium titanate (BaTiO3) ceramics [6-8]. The dielectric properties of these materials depend very much on grain size.

Ceramic materials of $Ba_{0.9}Li_{0.1}Ni_{0.05}$ by conventional state reaction were prepared. The high value for dielectric permittivity and low dielectric loss were obtained [9].

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The addition of cadmium to barium zirconium titanate reduces dielectric losses and increase value of piezoelectric charge constant d_{33}[10]. The legation additives used are Bi_2O_3 and H_3BO_3, which have relatively low melting temperature. They allow liquid phase synthesis of the ceramic materials and can stimulate the solid-state reactions. The density, the dielectric permittivity and the dielectric losses strongly depend of the sintered temperature.

2. EXPERIMENTAL DETAILS

The following composites have been derived in order to analyze the influence of bismuth trioxide Bi_2O_3 and boric acid H_3BO_3 on the non-linear properties of barium titanate ($BaTiO_3$), Table 1.

Table 1. Study composition.

№	Composite
1.	$BaTiO_3$ + 1mol%H_3BO_3
2.	$BaTiO_3$ + 2mol%H_3BO_3
3.	$BaTiO_3$ + 3mol%H_3BO_3
4.	$BaTiO_3$ + 4mol%H_3BO_3
5.	$BaTiO_3$ + 0.05mol%Bi_2O_3

The samples of ceramic materials were prepared by conventional mixed oxide solid state reaction method. The raw materials of extra pure grade $BaCO_3$, TiO_2, H_3BO_3 and Bi_2O_3 were weighed in appropriate proportion to obtain the stoichiometric ratio. The barium carbonate $BaCO_3$ and titanium dioxide TiO_2 are mixed with distilled water in zirconia vials, using zirconia ball, by Reach PM-100 planetary mill. Homogenization was done for duration of 4 hours. Homogenized mixtures dried at a temperature of 150°C after removing the zirconia ball. Prepared powder was pressed into pellets of 50 mm diameter and 20-25 mm thickness. As a binder have been using 3% water solution polyvinyl alcohol. The pellets of the made materials are sintered at a temperature of 900°C for 3 hours. After that, the pellets were crushed using planetary ball mill, after adding the necessary amounts of H_3BO_3 or Bi_2O_3.Milling powder was pressed into pellets of 10 mm diameter and 1.5-2 mm thickness and was calcined at a different temperature for 3 hours.

3. RESULTS AND DISCUSSION

An X-Ray Diffractometer with a monochromatic Cu-Kα radiation was used to ex-amine the crystal structure of the sintering ceramic materials over a 2θ angle from 20° to 80°.

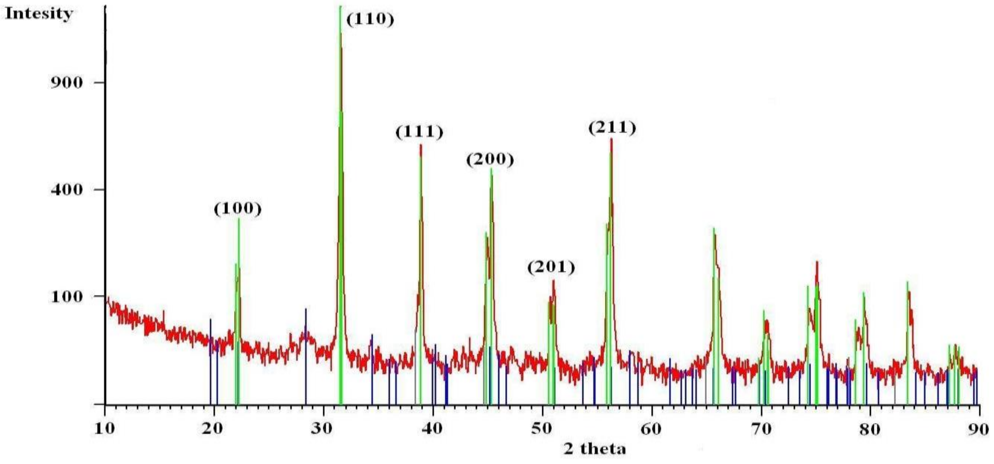

Fig. 1. X-ray diffractogram of $BaTiO_3$ doped with 2 mol% H_3BO_3 synthesized at temperature 1100°C.

Figure 1 shows the diffractogram of $BaTiO_3$, containing 2% of H_3BO_3, the synthesized at temperature 1100°C. From the diffractograms can be seen that the researching composition have single phase perovskite structure. Similar results were derived for the samples of the other analyzed composites, synthesized at different temperatures.

The Scanning Electron Microscope (SEM) was used for researching the microstructures of the surfaces. The average grain size of the specimen, doped with 2 mol% H_3BO_3, was about 1-2μm and there was no dependences on the variation of the sintering temperature (Figure 2).

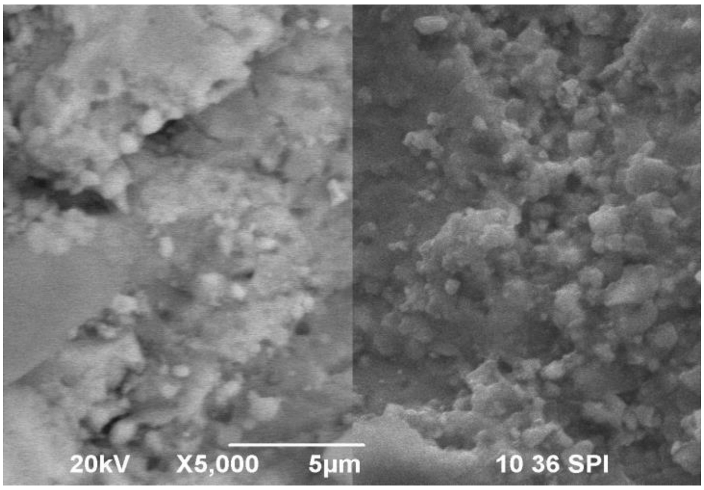

Fig. 2. a) and b) SEM of composite $BaTiO_3$ + 2mol% H_3BO_3, synthesized at temperature of 1250°C.

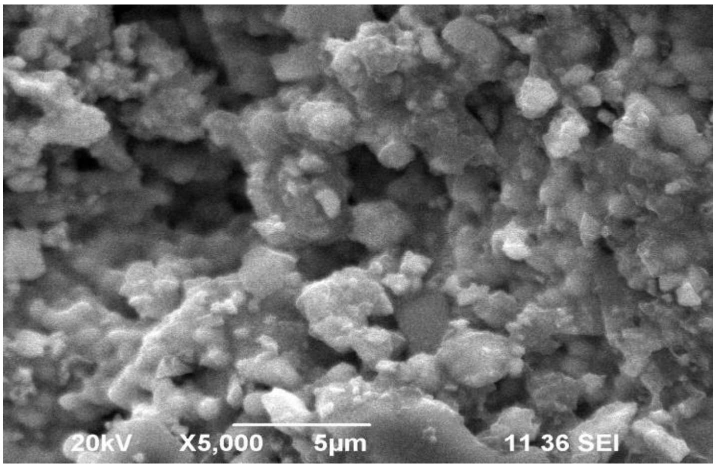

Fig. 3. SEM of composite $BaTiO_3$ + 3mol% H_3BO_3, synthesized at temperature of 1250°C.

The temperature dependencies of the dielectric permittivity have been analyzed. For those dependencies for a composite containing 2 mol % H_3BO_3, synthesized at different temperatures, phase transitions at Curie point have been observed. The phase transition is most evident at the highest sintering temperature. The higher quantity of the boric acid leads to decrease the values of the dielectric permittivity and to diffuse phase transition. For the materials sintered at low temperatures have been obtained diffuse phase transition. Table 2 shows the composites containing H_3BO_3, their dielectric permittivity and the Curie point for samples synthesized at different temperatures.

The temperature dependencies of the dielectric permittivity for compositions of doped barium titanate with 2 mol%H_3BO_3 and 0.05mol%Bi_2O_3 are showed in the Figure 4 and the Figure 5. The addition of 0.05mol%Bi_2O_3

to the barium titanate ($BaTiO_3$) significantly reduces the dielectric permittivity of the materials and leads to a diffuse phase transition.

Table 2. Dielectric permittivity and Curie temperature at a different sintering temperature.

Composite	$t_{sintering}$ (°C)	ε_r	Curie Point (°C)
$BaTiO_3$+1mol%H_3BO_3	1050	467	33
	1100	487	112
	1150	169	112
	1200	3627	111
	1250	3729	112
$BaTiO_3$+2mol%H_3BO_3	1050	916	104
	1100	836	106
	1150	1589	109
	1200	1427	107
	1250	2678	106
$BaTiO_3$+3mol%H_3BO_3	1050	384	110
	1100	192	120
	1150	510	120
	1200	1279	117
	1250	748	116
$BaTiO_3$+4mol%H_3BO_3	1050	468	107
	1100	562	105
	1150	385	115
	1200	965	114
	1250	927	113
$BaTiO_3$+0.05mol%Bi_2O_3	1050	972	103
	1100	958	120
	1150	420	117
	1200	1179	96
	1250	841	114

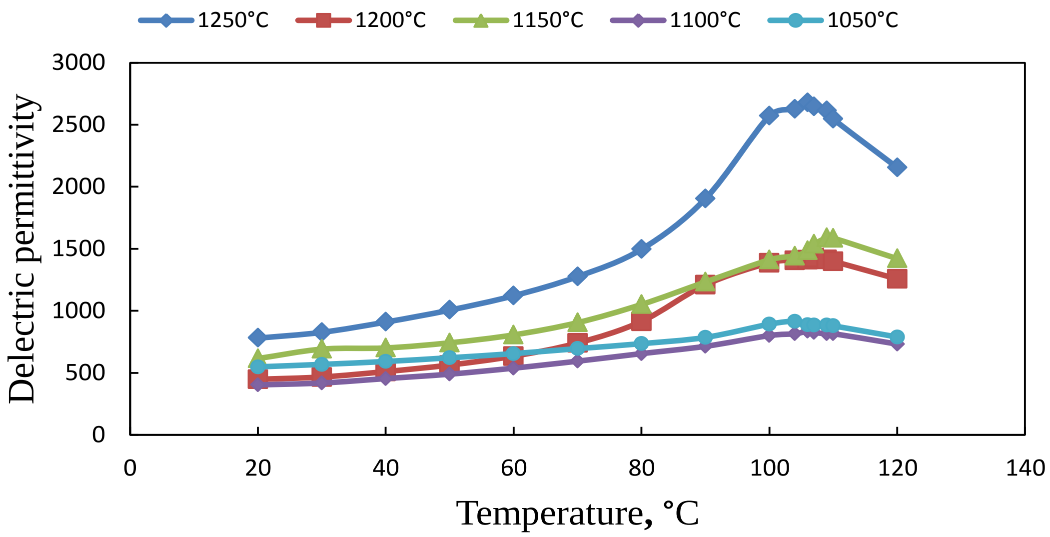

Fig. 4. Temperature dependencies of the dielectric permittivity for a composite containing 2mol% H_3BO_3.

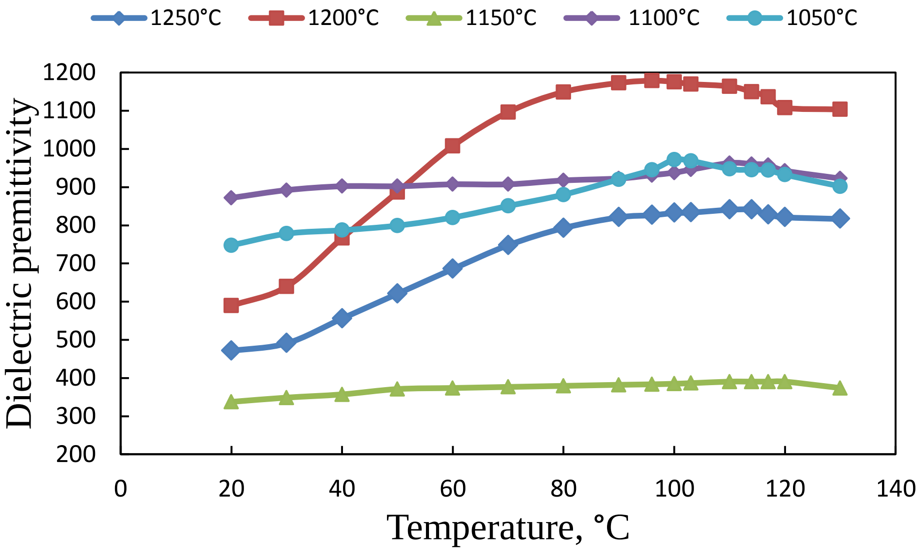

Fig. 5. Temperature dependencies of the dielectric permittivity for a composite containing 0.05mol% Bi_2O_3.

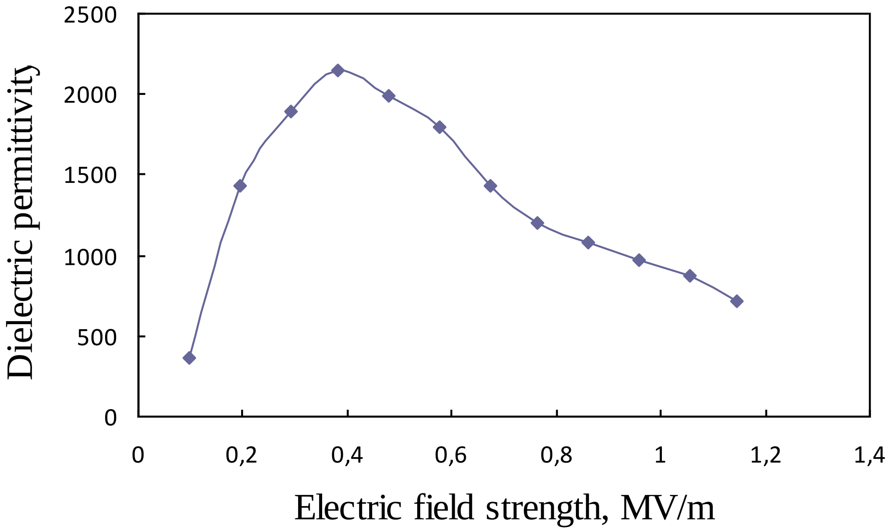

Fig. 6. Dependency of the dielectric permittivity on the electric field strength for materials $BaTiO_3$ +1mol%H_3BO_3, sintered at temperature1100ºC.

For evaluation of the nonlinear properties of the ferroelectrics, a non-linearity coefficient K is defined, which shows how many times the dielectric permittivity increases when the electric field strength increases compared to its initial value [11].

$$K = \frac{\varepsilon_{r\max}}{\varepsilon_{r\,initial}} \tag{1}$$

Figure 6 and Figure 7 present the dependencies of the dielectric permittivity on the electric field strength for the materials which have been obtained good non-linear properties.

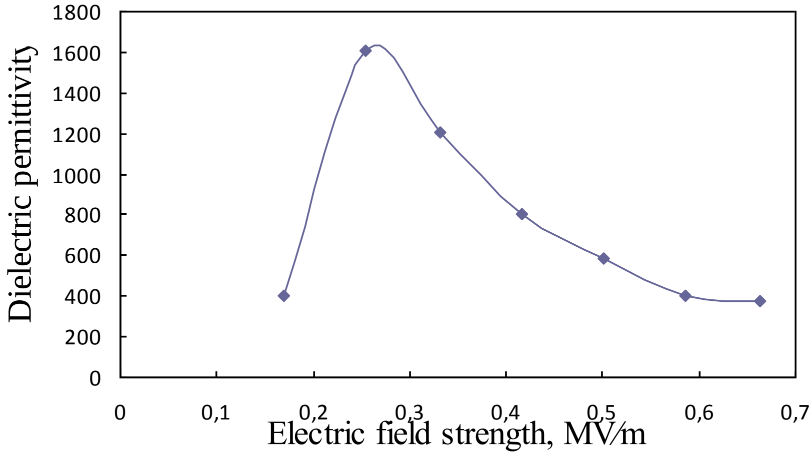

Fig. 7. Dependency of the dielectric permittivity on the electric field strength for materials $BaTiO_3$+3mol%H_3BO_3, sintered at temperature1100ºC.

For the non-linear ceramics, an important parameter is maximum values of the dielectric permittivity on the electric field strength. The values of the electric field for the analyzed materials, at which the dielectric permittivity reaches its maximum, are presented in Table 3. Table 3 shows a comparison of the non-linear properties of the ceramic materials, containing $BaTiO_3$ at different sintering temperatures.

Table 3. Comparison of the non-linear properties of the ceramic materials, containing $BaTiO_3$ at different sintering temperatures.

Composite	$t_{sintering}$ (°C)	$\varepsilon_{rinitial}$	ε_{rmax}	K
$BaTiO_3$ + 1mol%H_3BO_3	1050ºC	2066,0	3305,6	1.6
$BaTiO_3$ + 1mol%H_3BO_3	1100ºC	358,5	2151,1	6,0
$BaTiO_3$ + 1mol%H_3BO_3	1150ºC	594,6	1486,6	2.5
$BaTiO_3$ + 2mol%H_3BO_3	1050ºC	1534,0	2679	1,7
$BaTiO_3$ + 2mol%H_3BO_3	1100ºC	593,1	2668,6	4,5
$BaTiO_3$ + 3mol%H_3BO_3	1100ºC	235,9	1603,5	6,8
$BaTiO_3$ + 3mol%H_3BO_3	1150ºC	423,9	1341,7	3,2
BaTiO3 +0,05mol%Bi_2O3	1050ºC	524	1563,0	3,1
BaTiO3 +0,05mol%Bi_2O_3	1150ºC	557	1115,9	2,1

The addition of H_3BO_3 to ceramic materials containing barium titanate leads to higher values of the non-linear coefficient compared to the addition of Bi_2O_3 to the same materials. The optimal sintering temperature for the first group of materials is 1100ºC, whereas for the materials doped with Bi_2O_3 that temperature is 1050ºC. Both of those additions significantly increase the non-linear properties of the barium titanate ($BaTiO_3$), but decrease the values of the dielectric permittivity. That increase is higher when was added Bi_2O_3.

The sintering temperature decreases by 200 – 250°C when H_3BO_3 и Bi_2O_3 are added to the barium titanate ($BaTiO_3$). That temperature is 1350 ºC for pure barium titanate ($BaTiO_3$). Simultaneously, the non-linear properties improve while the dielectric permittivity decreases.

4. CONCLUSIONS

Ceramic materials based on Barium titanate with 1,2,3 and 4 mol% H_3BO_3 as well as $BaTiO_3$ with 0.05 mol% Bi_2O_3, have been synthesized at temperatures 1050, 1100, 1150, 1200 and 1250ºC. The diffractograms show the synthesis of mono phase structure with reflexes typical for the barium titanate. According to SEM the structure of the materials is relatively homogeneous and the size of the beans is up to 10 μm.

For materials derived from $BaTiO_3$ doped with 1mol% and2mol% H_3BO_3 have been obtained high values of the relative permittivity sintered at higher temperatures. For these materials the phase transition are obvious.

For materials derived from $BaTiO_3$ doped with 0.05mol%Bi_2O_3 have been obtained the diffuse phase transitions at all temperature of sintered.

The most suitable materials for non-linear elements are the ceramics based on $BaTiO_3$, doped with H_3BO_3 and sintered at temperature 1100ºC.

REFERENCES

[1] Noh, H.J., Lee, S.G., Yoon, S.E., Park, S.M., Dielectric properties of Yb_2O_3 – doped barium strontium titanate thick films for microwave device applications, Journal Material Science, vol. 43, 2008, p. 3421-3416.
[2] Kamehara, N., Karihara, K., Effect of rare earth elements doping on the electrical properties of $(Ba,Sr)TiO_3$ thim film capacitor, VLSI Packaging Workshop of Japan, 2008, p. 113-116.
[3] Mahesh, M., Bhanu Prasad, V., James, A., Effect of sintering temperature on the microstructure and electrical properties of zirconium doped barium titanate ceramics, Journal Material Science: Material Electronics, vol. 24, 2013, p. 4684 – 4692.
[4] Liu, J., Gong, S., Jin, G., Zhai, Z., Zhao, Z., Luo, C., Jiang, Q., Influence of reoxidation on silica-containing barium titanate ceramics for PTRC thermistors prepared by tape casting, Journal Ceramics – Silicáty, vol.60, no.2, 2016, p. 58-62.
[5] Jain, A., Maikhuri, N., Rakesh, S., Pastor, M., Jha, A.K., Panwar, A.K., Microstructural and dielectric investigations of vanadium substituted barium titanate ceramics, Advanced Material Letters, vol. 7,no. 7, 2016, p. 567-572.
[6] Li, L., Fu, R., Liao, Q., Ji, J., Doping behaviors of NiO and Nb_2O_5 in $BaTiO_3$ and dielectric properties of $BaTiO_3$ - based X7R ceramics, Journal Ceramics International, vol.38, 2012, p. 1915-1920.
[7] Armstrong, T., Morgens, E., Maurice, A., Buchanan, R., Effects of zirconia on microstructure and dielectric properties of barium titanate ceramics, Journal American Ceramics Society, vol.72, no.4, 1989, p. 605-61.
[8] Lu, Y., Hao, H., Zhang, S., Liu, H., Su, C., Yao, Z., Cao, M., Microstructure and dielectric characteristics of Nb_2O_5 – doped $BaTiO_3$ – $(Bi_{1/2}\ Ti_{1/2})O_3$ ceramics for capacitor applications, Journal of the European Ceramics Society, vol. 37, 2017, p. 123-128.
[9] Alkathy, M., Gayam, R., Hazra, B.K., Raju, K.C., Effect of sintering on structural and physical properties of nickel and lithium co-substituted barium titanate ceramics, Journal Ceramics International vol. 43, 2017, p. 4937-4949.
[10] Bajpaj, K.K., Srenivas, K., James, O.P., James, A,R., Shukla, A.K, Influence of Cd on the electro-strain of barium zirconate ceramics, Journal Ceramics International, vol. 43, 2017, p. 1963-1967.
[11] Verbitkaya, T., Varicond, 1st edn. Gosenergoizdat, Moscow,1958, p. 62 (In Russian).