Influence of the Doping Additives on the Properties of the Synthesized Barium Titanate

Ivaylo Lazarov[1] and Anka Zheglova[2]

Abstract – **In this paper are investigated influence of the different doped additives on the properties of the synthesized barium titanate. For composition $BaTiO_3$ + 1mol%H_3BO_3 have been obtained the highest values for the density, relative shrinkage and the relative permittivity at the temperatures of sintering 1200°C and 1250°C. The adding of the 0.05mol%Bi_2O_3 and 0.05mol%SnO_2 increases the values of the relative permittivity. For these compositions is observe the diffuse phase transitions in the temperature dependencies of the dielectric permittivity.**

Keywords –**Barium titanate, Doping additives, Dielectric permittivity.**

I. Introduction

Barium titanate is one of the most studied ferroelectric materials due to its excellent properties and high values of the dielectric permittivity. $BaTiO_3$ – based ceramics are widely uses in manufacture of multilayer capacitors (MLCC)[1], thermistors[2], electric-field tunable devices[3], sensors[4] and piezoelectric actuators[5]. Barium titanate is typical ferroelectric material with perovskite tetragonal microstructure (ABO_3) at room temperature and the Curie of temperature about 120°C. When heated above the Curie of temperature, it passes from ferroelectric to parra-electric phase. It is structure changes from tetragonal to cubic.

Much efforts have been developed to improve its dielectric properties such as increase the dielectric permittivity and decrease the dielectric losses.In order toobtain the required dielectric properties of modified barium titanate ceramics are added various doped additives suchas MnO_2[6], NbO_2[7], Sn[8], W[9], Ca[10], Zr[11].The doped additives influence also on the homogeneity, the particle size, the density, the structural defects and Curie of temperature.

The aim of this study is to determine the influence of the doping additives on the properties of the synthesized barium titanate.

II. Experemental

Samples of the study compositions were prepared using solid-state reactionmethodtaking commercial barium titanate $BaTiO_3$. As doped additives are used boric acid H_3BO_3, bismuth trioxide Bi_2O_3 and stannic oxide SnO_2 such as the starting powders are in stoichiometric proportions. The starting powders in the required amounts have been homogenized in 3% of polyvinyl alcohol solution for 4 hours at planetary mill Pulvirisete 5. After drying the materials have been formed in the form of disks with diameter 11mm and thickness of 2-3mm., by compression at a pressure 300MPa. Synthesis was carried out in air for 2 hours at five different temperatures – 1050°C, 1100°C, 1150°C, 1200°C and 1250°C. After a mechanical treatment, silver electrodes have been formed by applying a coating of silver paste on the ceramic disks, calcined at the temperature of 900°C for 1h.

III. Analysis of the Results

A. Density and relative shrinkage

The results of the measured density at different sintering temperatures are presented in Fig.1 and are given in Table I. The density increases for compositions $BaTiO_3$ + 1mol%$H_3BO_3$and $BaTiO_3$+0.05mol%$SnO_2$with increasing the temperature of sintering. The density has maximum values for composition $BaTiO_3$+0.05mol%Bi_2O_3 at temperature of sintering 1200°C. At the temperature of sintering 1250°C the density decreases for this composition.

Table I
The values of the density at different temperatures of sintering for study compositions

Composition	$t_{sintering}$, [°C]	Density ρ, [g/cm³]
$BaTiO_3$+1mol%H_3BO_3	1050	3,41
	1100	3,67
	1150	4,12
	1200	5,52
	1250	5,61
$BaTiO_3$+0.05mol%Bi_2O_3	1050	3,9
	1100	5,18
	1150	5,25
	1200	5,28
	1250	4,18
$BaTiO_3$+0.05mol%SnO_2	1050	3,27
	1100	3,28
	1150	3,332
	1200	3,98
	1250	5,16

[1]Ivaylo Lazarov is with the Faculty of Electrical Engineering and Electronicsat Technical University of Gabrovo, 4 H. Dimitar Str, Gabrovo 5300, Bulgaria, E-mail:iv.lazarovt@mail.bg.

[2]Anka Zheglova is with the Faculty of Electrical Engineering and Electronicsat Technical University of Gabrovo, 4 H. DimitarStr, Gabrovo 5300, Bulgaria.

The highest values of the density have been obtained for composition $BaTiO_3$ + 0,05mol%Bi_2O_3 at low temperature of sintering. At high temperatures of sintering were obtained the highest values of the density for compositions $BaTiO_3$+1mol%H_3BO_3.

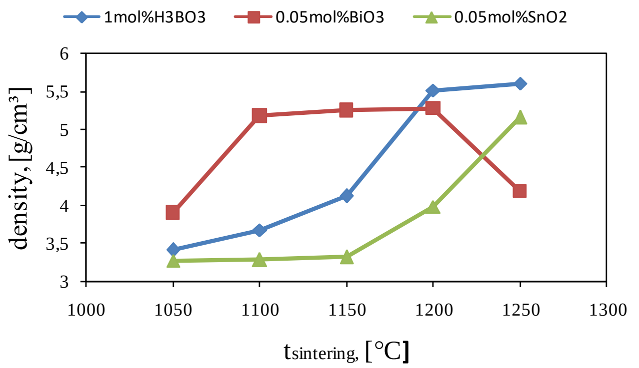

Fig. 1.Dependence of the density of the ceramic materials on the temperature of sintering

The results for obtained values of the relative shrinkage for study compositions are given in Table II.

TABLE II
THE VALUES OF THE RELATIVE SHRINKAGE AT DIFFERENT TEMPERATURES OF SINTERING FOR STUDY COMPOSITIONS

Composition	$t_{sintering}$, [°C]	relative shrinkage, [%]
$BaTiO_3$+1mol%H_3BO_3	1050	-1,82
	1100	-3,64
	1150	-7,27
	1200	-16,36
	1250	16,36
$BaTiO_3$+0.05mol%Bi_2O_3	1050	-4,55
	1100	-13,6
	1150	-13,6
	1200	-14,56
	1250	-7,27
$BaTiO_3$+0.05mol%SnO_2	1050	0
	1100	0
	1150	0
	1200	-5,45
	1250	-13,64

For composition $BaTiO_3$+0.05mol%SnO_2 do not observe relative shrinkage at low temperature of sintering. The relative shrinkage increases with increasing the temperature of sintering for composition $BaTiO_3$+1mol%H_3BO_3. For composition $BaTiO_3$+0.05mol%Bi_2O_3 have been obtained the maximum values of the relative shrinkage at the temperature of sintering 1200°C.

The highest values of the relative shrinkage have been obtained for composition $BaTiO_3$+1mol%H_3BO_3 at the high temperatures of sintering.

Fig.2 shows dependence of the relative shrinkage versus temperature of sintering.

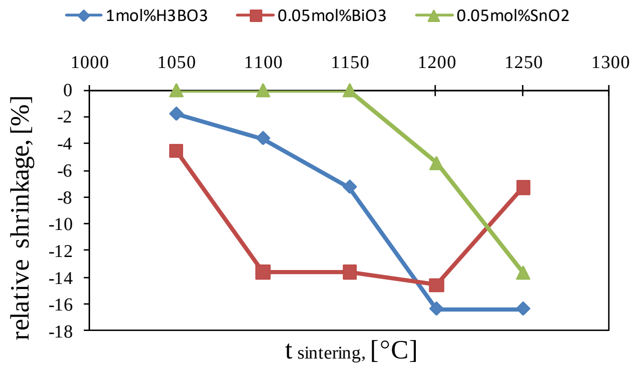

Fig. 2.Dependence of the relative shrinkage of the ceramic materials on the temperature of sintering

B. *Dielectric permittivity*

In the Fig.3 are showed the variation of the dielectric permittivity as a function of the temperature of sintering.

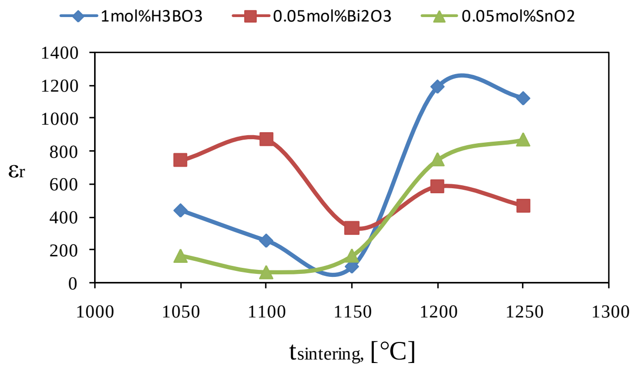

Fig.3. Dependence of the relative permittivity on the temperature of sintering

The highest values of the relative permittivity have been obtained for composition from doped with 1mol%H_3BO_3barium titanate at the temperatures of sintering 1200°C and 1250°C.The adding of 0.05mol%Bi_2O_3 to barium titanate reduces the temperature of sintering. The highest values of the dielectric permittivity have been obtained for this composition at low temperature of sintering.

The values of the relative permittivity at the Curie temperature and the Curie temperature for composition $BaTiO_3$+1mol%H_3BO_3 are given in Table III.

Fig.4.shows the temperature dependencies on the relative permittivity for doped with 1mol%H_3BO_3barium titanate.

It is found that dielectric permittivity have been the highest values for samples sintered at temperatures 1200°C and 1250°C. It is observed dielectric peaks in the temperature dependencies of the relative permittivity about 110°C. The diffuse phase transitions have been obtained for samples sintered at temperature 1050, 1100 and 1150°C.

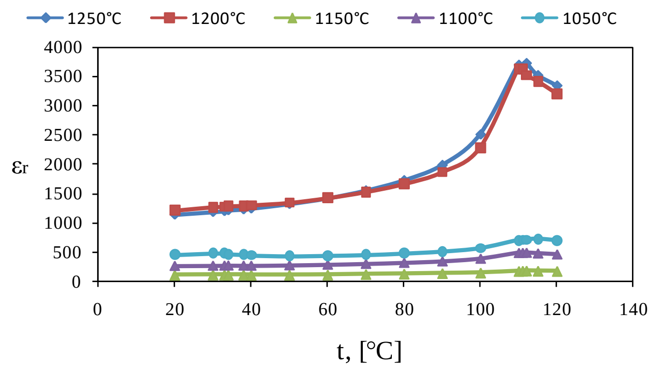

Fig.4. Temperature dependencies on the relative permittivity for composition $BaTiO_3$+1mol%H_3BO_3 at different temperatures of sintering

Table III

THE VALUES OF THE DIELECTRIC PERMITTIVITY AT THE CURIE TEMPERATURE AND THE CURIE TEMPERATURE FOR DOPED WITH 1MOL%H_3BO_3 BARIUM TITANATE

$t_{sintering}$, [°C]	max ε_r	Curie temperature, [°C]
1050	467	113
1100	487	112
1150	101	112
1200	3627	111
1250	3729	112

The temperature dependencies for composition $BaTiO_3$+0.05mol%Bi_2O_3 are shown in Fig.5.

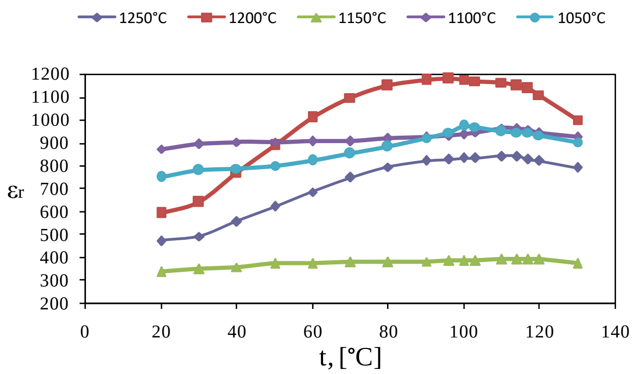

Fig.5. Temperature dependencies on the relative permittivity for composition $BaTiO_3$+0.05mol%Bi_2O_3 at different temperatures of sintering

The adding of 0.05mol%Bi_2O_3 leads to reduce the temperature of sintering. It is observed the diffuse phase transitions for the temperature dependencies at all the temperature of sintering. The values of the relative permittivity at high temperature of sintering are lower than for composition from doped with 1mol%H_3BO_3 barium titanate.

The values of the relative permittivity at the Curie temperature (max ε_r) and the Curie temperature for composition $BaTiO_3$+0.05mol%Bi_2O_3 are given in Table IV.

Table IV

THE VALUES OF THE DIELECTRIC PERMITTIVITY AT THE CURIE TEMPERATURE AND THE CURIE TEMPERATURE FOR DOPED WITH 0.05MOL%Bi_2O_3 BARIUM TITANATE

$t_{sintering}$, [°C]	max ε_r	Curie temperature, [°C]
1050	972	103
1100	958	120
1150	420	117
1200	1179	96
1250	841	114

The temperature dependencies for composition $BaTiO_3$+0.05mol%SnO_2 are shown in the Fig.6.

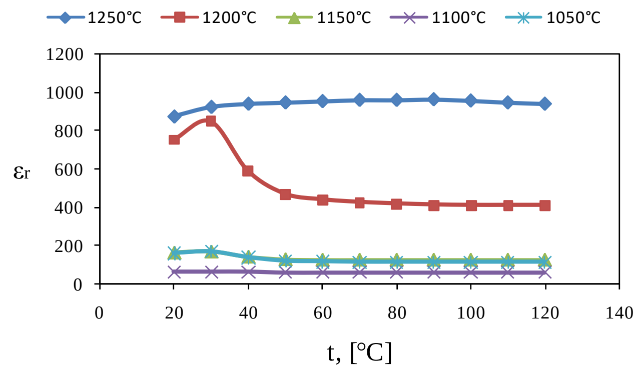

Fig.6. Temperature dependencies on the relative permittivity for composition $BaTiO_3$+0.05mol%SnO_2 at different temperatures of sintering

The highest values of the dielectric permittivity have been obtained for samples, sintered at temperature 1250°C. It is observed diffuse phase transitions. For samples sintered at temperature 1200°C have been obtained lower the values of the dielectric permittivity, but on the temperature dependence have been found dielectric peak at the temperature near to the room temperature. The values for the dielectric permittivity are the lowest than all studies compositions.

The values of the relative permittivity at the Curie temperature (max ε_r) and the Curie temperature for composition $BaTiO_3$+0.05mol%SnO_2 are given in Table V.

Table V

THE VALUES OF THE DIELECTRIC PERMITTIVITY AT THE CURIE TEMPERATURE AND THE CURIE TEMPERATURE FOR DOPED WITH 0.05MOL%SnO_2 BARIUM TITANATE

$t_{sintering}$, [°C]	max ε_r	Curie temperature, [°C]
1050	171	32
1100	62	40
1150	169	31
1200	865	31
1250	962	89

IV. Conclusion

Doped BaTiO3 ceramics were prepared by a solid state reaction method are investigated. The adding of 1mol%H_3BO_3 leads to obtain the higher values of the density, the relative shrinkage and the dielectric permittivity at temperatures of sintering 1200ºC and 1250ºC.The diffuse phase transitions have been obtained for doped with 0.05mol%Bi_2O_3 and 0.05mol%SnO_2 barium titanate. The adding of 0.05mol%Bi_2O_3 reduces the temperature of sintering.

References

[1] C.Ma, X.H.Wang, R.Z.Chen, L.T.Li, Z.I.Gui, "The structure and dielectric properties of low temperature sintering barium titanate based x7r ceramics", Journal of Electroceramics, vol.21, pp.242-245, 2008.

[2] M.Wegman, R.Brönnimann, F.Clemens, T.Graurle, "Barium titanate-based PTCR Thermistors fiber:Processing and properties", Sensors and Actuators A:Physical, vol.135, no. 12, pp. 394-404, 2007.

[3] T.Wang, X.M.Chen, H.H.Zheng,"Dielectriccharacterristics and tenability of barium stannatetitanate ceramics", Journal of Electroceramics, vol.11. pp. 173-178, 2013.

[4] J.Wang, H. Wan, Q. Lin," Properties of a nanocrystalline barium titanate on silicon humidity sensor", Measurement Science and Technology, vol. 14, no 2, pp.172-175, 2003.

[5] J.Gao, D.Xue, W.Liu, C.Zhou, X.Ren, "Recent progress on $BaTiO_3$-based piezoelectric ceramics for actuators application", Actuators, vol.6, pp. 1-20, 2017.

[6] D.Sitko, W.Bak, M.Garbartz-Glos, M.Antonova, I.Jankowska-Sumara, "Effect of MnO_2 doping on the dielectric properties of barium titanate ceramics", Ukrainian Journal of Physical-Optics, vol.13, pp.34-43, 2012.

[7] Y.Yan, S.R.Zhang, X.H.Zhou, B.Tang, "Effects of Nb_2O_5 doping on the microstructure and the dielectric temperature characteristics of barium titanate ceramics", Journal of Marerials Science, vol.44, no.14, pp.3751-3757.

[8] S.A.Solopan, A.G.Belous, O.I. V'yunov, L.L.Kovalenko, "$BaTi_{1-x}Sn_xO_3$ solid solution: Solid –phase and sol-gel syntheses and characterization", Russian Journal in Organic Chemistry, vol.53, no. 2, pp. 197-203.

[9] S.Devi, S.Jain, A.K.Jha, "Effect of sintering temperature on dielectric properties of tungsten doped barium titanate",17th IEEE International Symposium on the applications of ferroelectrics, vol.3, pp.1-5 , 2008.

[10] M.R.Panigrahi, S.Panigrahi, "Synthesis and microstructure of Ca-doped $BaTiO_3$ceramics prepared by high-energy ball milling", Physica B: Condensed Matter., vol. 404, no. 21, pp. 4267-4272, 2009.

[11] M.Aghayana, A.Khorsand.Zak,M.Behdania, A.ManafHashimc, "Sol-gel combustion synthesis of Zr-doped $BaTiO_3$nanopowders and ceramics: Dielectric and ferroelectric studies", Journal Ceramic International, vol.40, pp. 16141-16146, 2014.