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The Influence of $CaZrO_3$ on Microstructure and Dielectric Properties of $BaTiO_3$

V.Mitic,V.B.Pavlovic[1],B.Stojanovic[2],Z.Nikolic[3]

Faculty for Electronic Engeneering, Serbia, vmitic@eierc.com
[1]Faculty for Agriculture, Serbia,vlaver@beotel.yu
[2]Center for Multidisciplinary studiesUB,Serbia,biljana@ibiss.bg.ac.yu
[3]Faculty for Physics, Serbia

The microstructure and dielectric properties of barium titanate doped with $CaZrO_3$ were studied. Microstructural investigation was carried out by scanning electron microscopy, using digital pattern recognition method. Distribution of grain size and porosity were followed on samples with different additives contents and with various sintering densities. Several different types of grains shape and grains size were determined. First grains showed polygonal shape, other ones were in almost rounded shape, connecting together and forming very irregular configuration. Third kind of grains showed spiral grain growth. By EDS analysis was found the various concentration of Zr in different shape type of grains.It was noticed that that the increase of amount of $CaZrO_3$ .The results of capacitance and loss tangent as a function of different additive contents and samples were presented.The frequency characteristics of capacitance, loss tangent and impendance were carry out. The effect of concentration of $CaZrO_3$ on dielectrical properties od doped barium titanate was analysed.
Key words: $BaTiO_3$, $CaZrO_3$, microstructure, dielectric properties

INTRODUCTION

It is well known that barium titanate based materials provide properties that are important for a variety of electrical and electronical applications [1]. To achieve better electrical properties of these materials, optimisation of the process parameters has to be obtained. Since grain size and distribution considerably affect electrical properties of barium titanate based materials, correlation of their microstructure and electrical properties has been investigated by numerous authors [2-4]. Gained results relate to the distribution and the size of grains and pores, to the degree of interior strain within grains boundary, and the structure of grains boundary. It has been shown that electrical properties of undoped and doped $BaTiO_3$ ceramics are mainly controlled by barrier structure, domain motion of domain boundaries and the effects of internal stress in the grains [5-6].

In order to obtain temperature stable dielectric behaviour of barium-titanate based ceramics either small grained microstructure [7], or the microstructure with core-shell grains has to be achieved. The second type of microstructure can be obtained with the addition of ZrO [8].

In this paper we have reported experimental results of the investigation of the influence of $CaZrO_3$ on microstructural and electrical properties of $BaTiO_3$ ceramics.

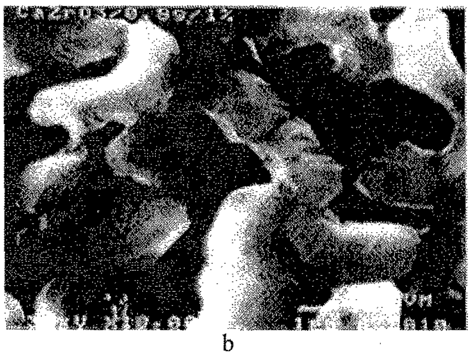
EXPERIMENTAL PROCEDURE

Samples of $BaTiO_3$ with small amounts of $CaZrO_3$ (0.5, 1, 1.5 wt%) have been investugated. Samples were sintered in the tunnel furnace CT-10 MURATA at 1300 °C for 2 hours. Microstructure characterization has been carried out by scanning electron microscope (JEOL-JSM-T20). Grain size distribution and porosity of the samples were investigated by digital pattern recognition method. Elemental analysis of the grains was performed by EDS QX2000S. Capacitance and loss tangent of the samples were measured in the frequency range from 1-20 KHz .

RESULTS AND DISCUSSION

In order to understand the microstructural evolution of $CaZrO_3$ doped $BaTiO_3$, the study of the change of microstructural parameters as a function of concentration of additive has been performed. In Figs. 1 a)-d) SEM microphotographs of sintered $BaTiO_3$ ceramic samples with 0.5, 1.0 and 1.5 wt% of $CaZrO_3$ are shown.

a



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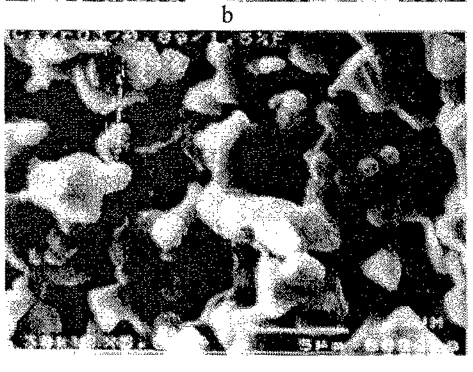

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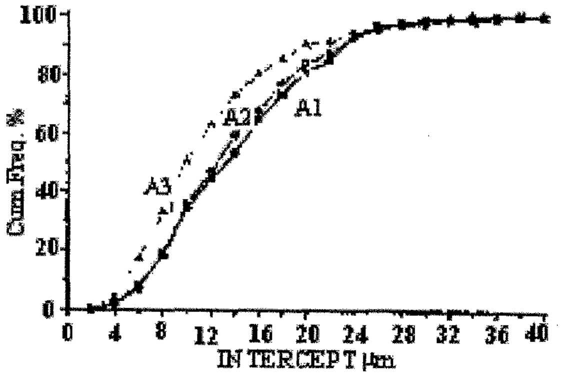


d

Fig.1. Microstructures analysis of $BaTiO_3$ doped with $CaZrO_3$ of wt % a) 0.5, b) 1.0, c) 1.5

Two different type of grains were detected: polygonal ones and oval "glue together" grains. For polygonal grains, the EDS spectra did not show the presence of Zr, while a larger quantity of Zr is detected for irregular grains. The maximum grain size is up to 5 μm, while the average grain size is less than 2 μm. The results of maximum (a_{max}), minimum (a_{min}) and average (a_{av}) grain size and pores volume ratio percentage (V_p(%)) for $BaTiO_3$ ceramic samples with 0.5, 1.0 and 1,5 wt.% of $CaZrO_3$ are given in Table 1. It can be noticed that the increase of the amount of $CaZrO_3$ effected the lowering of grain size values. Investigation of the porosity of the samples showed that the samples were not consolidated well, particularly in the previous process of powders mixing, forming and finally in the process of sintering. Thus, some $BaTiO_3$ particles could be far from the additive particles, requiring large diffusion paths for the access of Zr and Ca ions in the $BaTiO_3$ grains. It is known that in order to obtain more homogeneous additive distribution, such diffusion phenomena require rigorous thermal treatments.

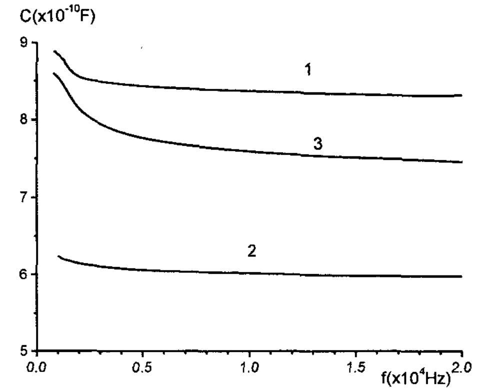
Table 1. Stereological parameters of the samples of $BaTiO_3$ sintered with $CaZrO_3$

$BaTiO_3$-$CaZrO_3$	a_{min}(μm)	a_{max}(μm)	a_m(μm)	V_v(%)
0.5%-IIA1	0.21	4.17	1.41	21.4
1.0%-IIA2	0.12	3.38	1.36	25.7
1.5%-IIA3	0.08	3.92	1.15	22.7

According to these results two opposite process during sintering of $BaTiO_3$ with $CaZrO_3$ could occur. The first one enhances sintering process, and ends with formation of core shell structure with $BaTiO_3$ core and Zr-modified $BaTiO_3$ shell [11]. The opposite one is the substitution of Ba ions with Ca ions, during which Ca ions acted as grain growth inhibitors.

Important electrical properties such as capacitance, loss tangent and impedance were correlated with different additive concentration. The diagram of capacitance vs. frequency for the samples sintered with different concentration of additive is shown in (Fig. 2). The obtained capacitance frequency curves show almost stable values in the observed frequency region. It can be noticed that the highest values of capacitance correspond to the samples sintered with 0.5 wt.% of $CaZrO_3$ and that capacitance decreased as the concentration of $CaZrO_3$ increased.

The loss tangent frequency characteristics show decrease in the whole frequency region, from the value of 0.32 towards 0.02 (Fig. 2b). The optimal loss tangent characteristic (the less loss tangent values) is obtained for the sample with 0.5 wt.% of $CaZrO_3$. The magnitude of the impedance vs. frequency for the samples sintered with different concentration of additive is presented in Fig 2c.



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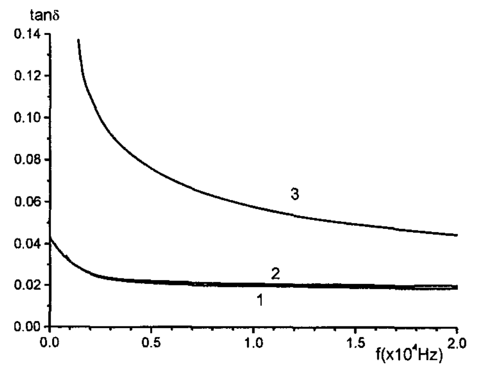

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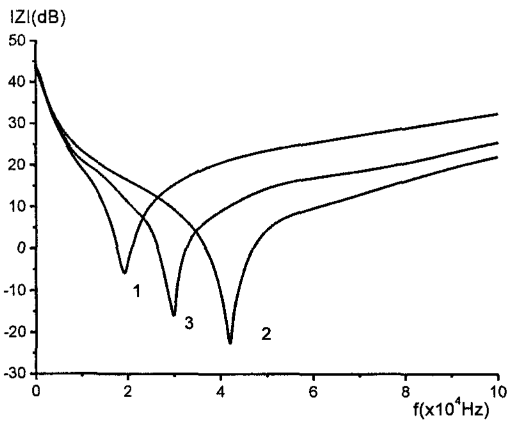

c

Fig.2. Capacitance vs frequency a) the loss tangent frequency characteristics b) and the magnitude of impedance vs. ferquency c) of doped $BaTiO_3$ 1) 0.5% $CaZrO_3$,

The optimal frequency characteristic is obtained for the samples sintered with 1 wt.% of $CaZrO_3$. Any further increase or decrease of the concentration of additive shifts the resonant peak towards lower frequencies, which reduces the area where the samples behave as a capacitor.

CONCLUSION

The influence of $CaZrO_3$ on microstructure and electric properties of $BaTiO_3$ ceramics has been studied. It was noticed that the increase the concentration of additive for the samples with the same initial density reduced the grain size. Two types of grains are observed, polygonal ones with absence of Zr and irregular ones, with a high quantity of Zr. The best properties from the view point of the capacitance and loss tangent values were obtained for the samples sintered with 0.5 wt.% $CaZrO_3$. Considering these results, prognosis of dielectric properties of $BaTiO_3$ ceramic materials, should be based on selection of optimal consolidation conditions and on obtaining the adequate microstructure.

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