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The Effects of Additive on Microstructure and Electrical Properties of $BaTiO_3$ Ceramics

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Abstract: In this paper comparative investigations of microstructure and dielectric properties of $BaTiO_3$ ceramics doped with 1.0 wt% of Nb_2O_5, $MnCO_3$ and $CaZrO_3$ have been done. $BaTiO_3$ samples were prepared using conventional method of solid state sintering at 1300^0C for two hours. Two distinguish microstructural regions can be observed in sample doped with Nb_2O_5. The first one, with a very small grained microstructure and the other one, with a rod like grains. In $MnCO_3$ and $CaZrO_3$ doped ceramics the uniform microstructure is formed with average grain size about 0.5- 2µm and 3-5µm respectively. The highest value of dielectric permittivity at room temperature and the greatest change of permittivity in function of temperature were observed in $MnCO_3/BaTiO_3$. In all investigated samples dielectric constant after initially large value at low frequency attains a constant value at $f \geq 6$kHz. A dissipation factor is independent of frequency greater than 10 kHz and, depending of systems, lies in the range from 0.035 to 0.25. At temperatures above Curie temperatures, the permittivity of all investigated samples follows a Curie-Weiss law. A slight shift of Curie temperature to the lower temperatures, in respect of Curie temperature for undoped $BaTiO_3$, was observed in all investigated samples.

Keywords: Doped $BaTiO_3$ ceramics, Dielectric properties, Microstructure.

1 Introduction

Barium titanate with different additives and dopants is one of the most useful ferroelectric materials suitable for wide fields of application [1-3] such as multilayer capacitors, thermistors, varistors and energy converting systems.

$BaTiO_3$ powder is usually mixed with various types of additives in order to obtain the better performances and a good control over a grain size and electrical characteristics of ceramics. It has been found that the dielectric properties of polycrystalline $BaTiO_3$ depend in a great extent on the grain growth during sintering and on additive type and concentration [4-6].

For the application of doped $BaTiO_3$ ceramics as a capacitor material, apart from a good density, a high dielectric constant and low loss factor have to be achieved. A high

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and stable dielectric constant over a broad temperature range usually requires a homogeneous and fine-grained microstructure with a compositional heterogeneity inside the grains, i.e. the core-shell structure [6]. The main factors that must to be taken into account during processing of ceramics are the homogenisation of $BaTiO_3$ powder with a suitable doping concentration, the sintering temperature and time.

Among the dopants that are used to modify the dielectric and semiconducting properties of $BaTiO_3$, niobium is the most useful donor dopant because it can be incorporated in $BaTiO_3$ lattice as Nb^{5+} at Ti^{4+} sites [7-9]. Depending on Nb concentration, $BaTiO_3$ may exhibit semiconducting or insulating properties. It has been reported that if a doping concentration exceeds a certain limits (0.5 %) [6] a dramatic decrease in grain size is occurred, thus leading to the change from semiconducting $BaTiO_3$ to insulator. K. Kowalski et all [7] reported that up to 6 at% Nb^{5+} can be incorporated into $BaTiO_3$ lattice according to the formula $Ba[Ti_{(1-5x)}Nb_x]O_3$.

Barium and titanium atoms can be replaced respectively by calcium and zirconium atoms. Hence, it is presumed that the addition of calcium and zirconium atoms resulted in the formation of $Ba_xCa_{1-x}Ti_yZr_{1-y}O_3$ solid solution. The addition of CaO effectively prevents the grain growth, improves the electromechanical properties and increases the temperature region where the tetragonal phase is stable [10], while ZrO_2 broadens the dielectric peak without affecting a loss factor [11].

The influence of Mn on the electrical and semiconducting properties of $BaTiO_3$ has been widely investigated [12, 13]. MnO or MnO_2 are frequently added to $BaTiO_3$ together with other additives in order to reduce the dissipation factor. It is well known that Mn belongs to the unstable acceptor dopants since it can be easily oxidized from Mn^{2+} to Mn^{3+} or Mn^{4+}. It was suggested that of the all form of manganese ion the Mn^{3+} ion is the most important no matter what form of manganese is introduced [13-15]. Mn ions as acceptor, incorporated at Ti^{4+} sites, reduce the oxygen vacancies. By the reducing the concentration of oxygen vacancies, diffusion of O^{2-} ions is retarded and hence the grain growth is inhibited. In high quality PTC- thermistors Mn ions, segregating at the grain boundaries affect in a great extent the PTC effect.

The purpose of this paper is a comparative investigation of the effects of Nb_2O_5, $MnCO_3$ and $CaZrO_3$ on the microstructure and dielectric properties of $BaTiO_3$ ceramics. The dielectric properties were investigated in function of frequency in the range of 1-20 kHz. The variation of dielectric constant with temperature was measured in temperature interval from 20 to 200°C.

2 Experimental

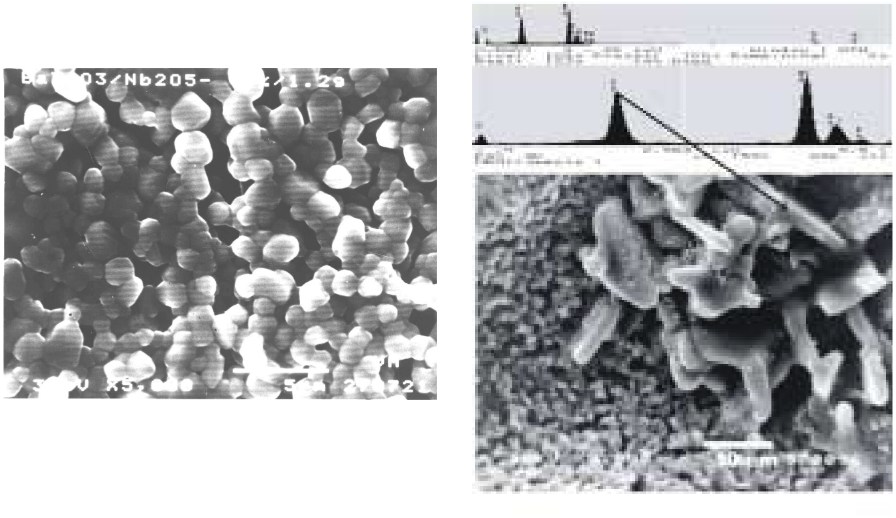
The doped $BaTiO_3$ specimens used for this investigation were prepared by a conventional solid state reaction technique. Commercial grade Nb_2O_5, $CaZrO_3$ and $MnCO_3$ were used as additive in the amount of 1.0 wt%. Starting powders of $BaTiO_3$ with Nb_2O_5 or $CaZrO_3$ or $MnCO_3$ were mixed in isopropyl alcohol by ball-milling, dried for several hours before being pressed into pellets under pressing pressure of P = 120 MPa. The pellets were sintered at 1300^0C in air atmosphere for two hours. The microstructures of the obtained ceramic materials were characterized by a scanning electron microscope

JEOL-JSM 5300 equipped with EDS (QX- 2000S) system. For electrical measurements silver paste was used on flat surfaces of the specimen. The capacitance and dielectric loss were measured using HP 4276 LCZ meter in a frequency range of 1-20 kHz. The variation of capacitance with temperature was measured in a temperature interval from 20 to 200°C.

3 Results and Discussion

3.1 Microstructure Investigations

The microstructures of Nb_2O_5 doped $BaTiO_3$ were shown in Fig.1. Two distinguish microstructure regions can be observed in this sample that differ not only in grain size but as well as in phase composition. The first one, with a very fine grained microstructure, grain size from between 1-2 μm (Fig.1a) and the other one, with a rod like grains, with high aspect ratio such as 5 and needle shape grains (Fig. 1b). Some residual porosity is evident after two hours of sintering but no evidence was found for the growth of abnormally large grains. The outstanding feature in these specimens is the presence of non homogeneous phase composition throughout the specimens.



a) b)

Fig. 1 - *SEM micrographs of Nb_2O_5 doped $BaTiO_3$ ceramics, a) the region with a fine grained microstructure, b) SEM/EDS spectrum of the region with rod like and needle shape grains.*

The observation of the corresponding EDS spectrum indicated that the regions, which are rich in Nb ions, were associated with the parts of sample with elongated and needle shaped grains. Due to the nonuniform distribution of Nb and its segregation in the local part of samples the presence of nonferroelectric region leads to the decrease of dielectric permittivity. In our previous work it has been shown [14] that with the increase of Nb content over 1wt% the decrease of dielectric constant is more pronounced to that ones with lower content of Nb. It is for believed that the initial powder preparation process and insufficient mixing of starting powders resulted in inhomogeneous microstructure patterns.

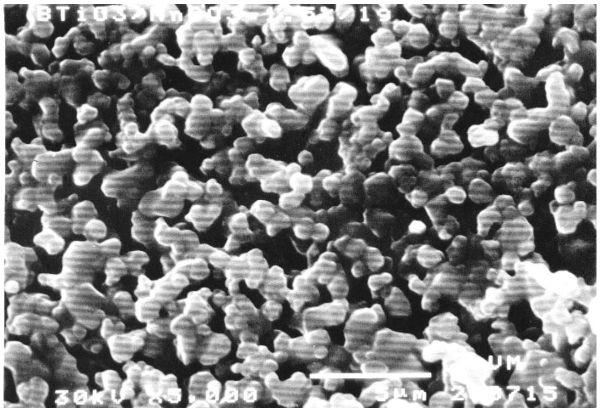
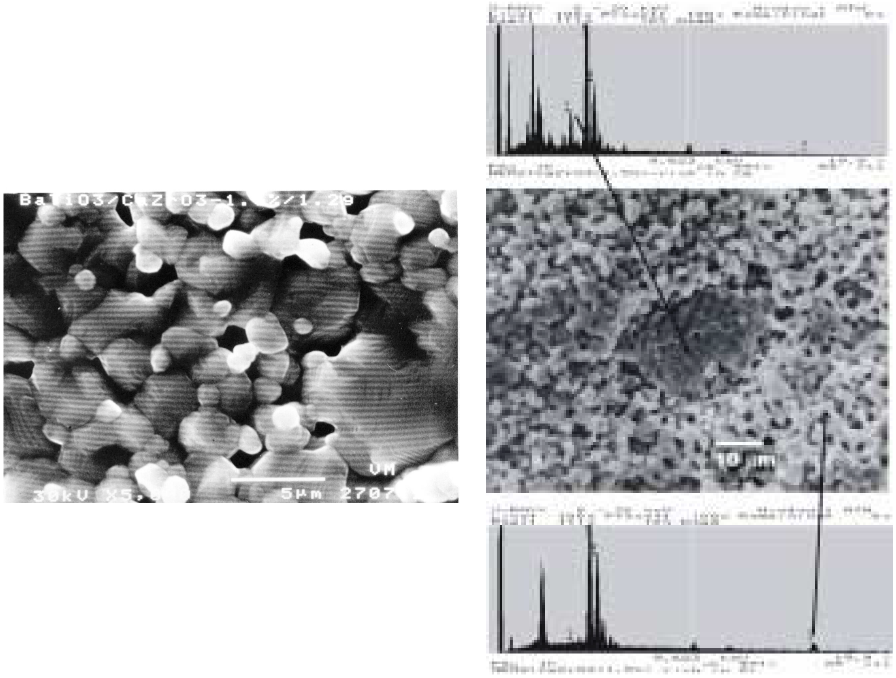


Fig. 2 - *SEM micrograph of $MnCO_3$ doped $BaTiO_3$ ceramics.*

$MnCO_3$ doped $BaTiO_3$ ceramics (Fig. 2) exhibits normal grain growth, a fairly uniform microstructure and homogeneous distribution of additives. In Mn/$BaTiO_3$ ceramics the average grain size from 0.5-2μm has been observed. The density of $MnCO_3$ doped $BaTiO_3$ is around 80 % of theoretical density. Although only few regions rich in Mn have been detected by EDS analysis, their influence on the uniformity of microstructure was negligible, as reported in [15].

Regarding the microstructure of $CaZrO_3$ doped $BaTiO_3$ sintered at 1300^0C a fairly uniform microstructure and normal grain growth has been observed. The average grain size in $CaZrO_3$ doped $BaTiO_3$ is around 3μm, although some grains size of 5μm are also present, as can be seen in Fig.3a. The regions with polygonal grains shown in fig. 3a, are characterized by a homogeneous phase composition. The sintering density of these specimens is 85% of theoretical density. Similar to the specimens with Nb_2O_5 as additive, in $BaTiO_3$ specimens with $CaZrO_3$ it has been found that the phase composition was not uniform throughout the specimens.

According to the EDS spectra (Fig.3b), some Ca or Zr rich regions were detected. The additive rich phases are formed in local regions due primarily to the insufficient homogenisation of starting powders. For polygonal grains, the EDS spectrum did not show the presence of Zr, while a considerable quantity of Zr is detected for irregular grains (Fig.3b). The presence of chemically inhomogeneous system in $CaZrO_3$/$BaTiO_3$ samples brings about the decrease of dielectric constant compare to the same one in $MnCO_3$/$BaTiO_3$ ceramics.



a) b)

Fig. 3 - *SEM micrographs of $CaZrO_3$ doped $BaTiO_3$ ceramic, a) uniform microstructure, b) SEM/EDS spectra indicating Ca and Zr rich regions*

3.2 Electrical Properties

The observed microstructure features together with the type of additive have a direct influence on the dielectric properties of doped $BaTiO_3$. The dielectric constant and loss factor are shown in Figs. 4 and 5 as a function of frequency for various type of additive.

The highest value of dielectric permittivity at room temperature (ε_r=1750) and the greatest change of permittivity in function of frequency was observed in $MnCO_3$ doped $BaTiO_3$ ceramics. Dielectric constant in $CaZrO_3$/ $BaTiO_3$ samples at room temperature is 1470. In $CaZrO_3/BaTiO_3$ sample, where a chemically inhomogeneous system is formed, the overall dielectric behaviour is governed by two different microstructure regions (Ca or Zr rich regions), thus leading to the decreasing of dielectric constant compare to the same one in $MnCO_3/BaTiO_3$ ceramics. The lowest value of dielectric constant of only 1330 is noticed in Nb_2O_5 doped $BaTiO_3$ samples. Due to Nb rich regions a significant part of sample exhibits a nonferroelectric behaviour of material.

In all investigated samples dielectric constant after initially large value at low frequency attains a constant value at f≥6kHz.

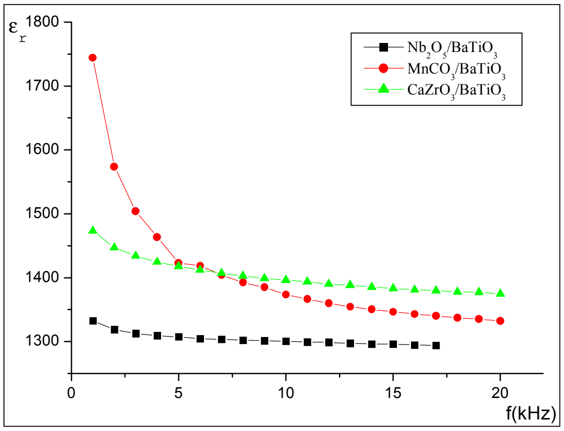


Fig. 4 - *Dielectric constant of modified $BaTiO_3$ ceramics in function of frequency*

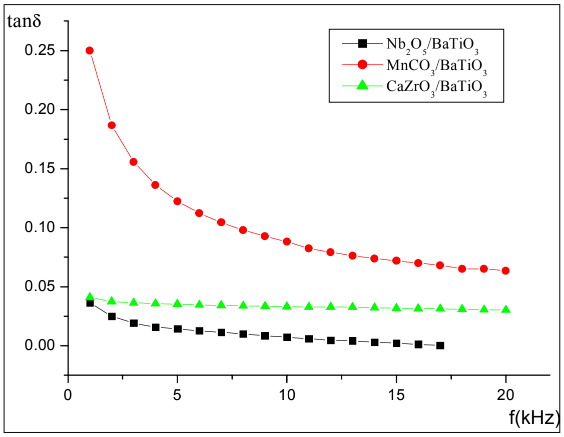


Fig. 5 - *Dielectric loss of modified $BaTiO_3$ ceramics in function of frequency*

Regarding the loss factor, a greatest value of loss factor (tanδ) and the greatest change in function of frequency was detected in $MnCO_3/BaTiO_3$ (Fig.5). Low values of *tanδ*, ranged from 0.035 for Nb_2O_5 doped $BaTiO_3$ to 0.25, for $MnCO_3$ doped $BaTiO_3$.

The influence of appropriate additive on the dielectric behaviour of doped $BaTiO_3$ can be analysed through permittivity–temperature curves shown in Fig.6.

In general, the permittivity-temperature response and a sharp phase transition, from ferroelectric to paraelectric phase at Curie temperature, are observed for $MnCO_3/BaTiO_3$ and $CaZrO_3/BaTiO_3$ samples. In $Nb_2O_5/BaTiO_3$ samples two different microstructure regions, where a chemically inhomogeneous systems are formed, together with a considerable amount of paraelectric phase the already existing at temperature below Curie temperature, govern the overall dielectric behaviour.

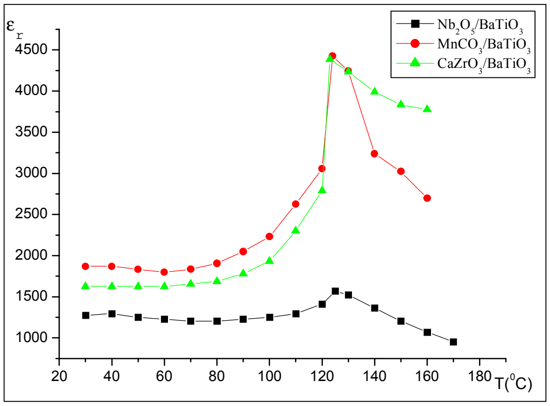


Fig. 6 - *Dielectric constant of modified $BaTiO_3$ ceramics in function of temperature*

A slight shiff of Curie temperature, in respect of Curie temperature for undoped $BaTiO_3$, was observed in all investigated samples as can be seen in Table 1. The amount of 1.0wt% of additive, since it was not uniformly distributed into the samples, has a small effect on the intrinsic dielectric parameter such as Curie temperature. However, the change in permittivity from 1750 to 4500 at Curie temperature for $MnCO_3$ doped $BaTiO_3$ indicates that the difference in dielectric behaviour is due partly to the grain size and certainly partly to the variation of Mn^{2+} fraction in (Mn^{3+} +Mn^{4+}).

A flat dielectric response in transition zone is observed for Nb_2O_5 doped $BaTiO_3$ in which paraelectric regions significantly reduce the dielectric permittivity. In $CaZrO_3$ doped $BaTiO_3$ the variation in dielectric permittivity at Curie temperature can be related to the synergistic effect of Ca and Zr ions, which is more distinct at higher temperature.

Table 1

Dielectric parameters of modified $BaTiO_3$ ceramics

Additives	$BaTiO_3$		
	Nb_2O_5	$MnCO_3$	$CaZrO_3$
[*Tc*] Curie temperature (°C)	125	123	122
ε_r at room temperature (f=1kHz)	1330	1750	1470
ε_r at Curie temperature	1500	4500	4300
[*C*] Curie constant (x10 $^{-5}$K)	1.008	2.337	5.490
[*C*] Curie constant for undoped $BaTiO_3$ (x10 $^{-5}$K)	2.09		
Tc for undoped $BaTiO_3$ (°C)	130		

The permittivity behaviour above Curie temperature for all samples can be characterized by the Curie-Weiss law

$$\varepsilon_r = \frac{C}{T - T_0} \qquad (1)$$

where C is Curie constant and T_o Curie-Weiss temperature, which is close to the Curie temperature.

According to the Curie–Weiss law, $1/\varepsilon_r$ temperature curves are fitted and corresponding Curie constants are calculated. Nevertheless of the additive type no deviations from Curie-Weiss law were detected. The Curie constants and related dielectric parameters are given in Table 1.

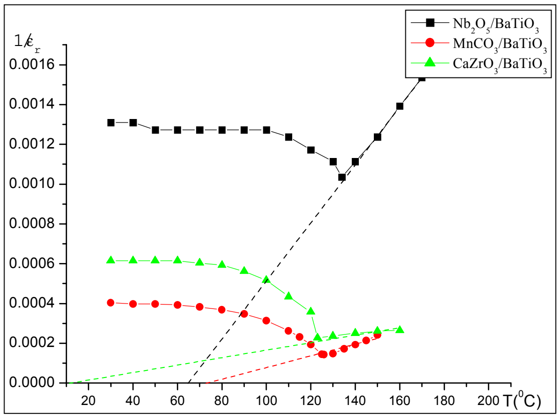


Fig. 7 - *Reciprocal values of ε_r in function of temperature*

A great exception of Curie constant in $CaZrO_3$ doped specimens (C=5.49) to that ones calculated in Nb_2O_5 or $MnCO_3$ doped $BaTiO_3$ (1< C < 2.33) can be contributed to the synergistic effect of Ca and Zr ions during sintering of $BaTiO_3$. The Zr ions lead to the formation of core-shell structure, with $BaTiO_3$ core and Zr modified $BaTiO_3$ shell [6]. Ca ions, segregating at grain boundaries, act as grain growth inhibitors. Since the doped BaTiO3 samples exhibit a different dielectric behaviour it is for expected that the Curie constant would be very sensitive to the type and concentration of additive.

4 Conclusion

In this paper comparative investigations of microstructure and dielectric properties of ceramics doped with Nb_2O_5, $MnCO_3$ or $CaZrO_3$ have been done. Two distinguish microstructural regions can be observed in sample doped with Nb_2O_5. The highest value of dielectric permittivity at room temperature and the greatest change of permittivity in function of temperature were observed in $MnCO_3/BaTiO_3$, which is characterized by a fairly uniform microstructure with a homogeneous distribution of additive. The Curie temperature for all investigated samples is lower compare to undoped $BaTiO_3$ ceramics.

A linear decrease of dielectric constant with frequency up to 6 kHz has been noticed in all specimens. For frequency greater that 6 kHz the constant values of εr are obtained.

A dissipation factor is independent of frequency greater than 10 kHz and, depending of systems, is in the range from 0.035 for Nb_2O_5 to 0.25 for $MnCO_3$ doped ceramics. A slight shiff of Curie temperature to the lower temperatures, in respect of Curie temperature for undoped $BaTiO_3$, was observed in all investigated samples.

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