FACTA UNIVERSITATIS (NIŠ)
SERIES: ELECTRONICS AND ENERGETICS VOL. 9, NO. 2 (1996), 255–262

THE FREQUENT AND FERROELECTRIC $BaTiO_3$–CERAMICS CHARACTERISTICS

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Abstract. The systematic study of microstructural–electrical properties correlation has a great importance, especially from the point of view of modelling frequent and hysteresis characteristics in $BaTiO_3$–ceramics containing a controlled amount of additives. The influence of additives such as CeO_2 and $MnCO_3$ which affect both the grain size and dielectric properties has been investigated. The low hysteresis and $\tan\delta$ losses along with the high dielectric permittivity suggest that Ce and Mn improved the capacitor properties of doped $BaTiO_3$.

1. Introduction

There is a continuous and growing interest in the use of electronics ceramics materials as they are finding increasing roles in variety of devices, because of their combined dielectric, ferroelectric, semiconductor, and electrooptic properties [1–3]. Among the many types of ferroelectric materials for high quality capacitors, the barium-titanate ceramics are being ones of the most intensively investigated systems. For capacitor type application, the primary requirements are the high permittivity characteristics and a small temperature variation of permittivity over a wide temperature region. To achieve a temperature stable dielectrics, barium–titanate is usually doped with a variety of additives such as Bi, Ce, Zr, Nb, Dy, and others oxides, which enhance either sintering rate or densification degree [4–7]. The most of additives act as grain growth inhibitors, as it is known, that in the small grained ceramics the higher permittivity could be obtained [8]. The electrical properties, specific frequency and hysteresis characteristics may also be influenced by appropriate additives.

Manuscript received May 14, 1996.

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Among the additives which inhibit discontinuous grain growth and lower the sintering temperature are CeO_2 and $MnCO_3$ [9]. The high dielectric constant value together with low dielectric losses are the main characteristics of $BaTiO_3$ with CeO_2 and $MnCO_3$ as additives. It has been shown previously [10] that the capacitance do not change significantly in the wide region of temperature, and that the high dielectric constant could be achieved if both CeO_2 and $MnCO_3$ were present. For this reason the present study was undertaken to investigate the synergestic effect of both CeO_2 and $MnCO_3$ in different concentration ratio, on the dielectric properties of sintered compacts.

A part of this research is devoted to the investigation of the frequency characteristics of sintered compacts owing to the presence of $MnCO_3$ and CeO_2.

2. Experimental

The polycrystalline samples were prepared and sintered by a conventional mixed oxides process, starting from high purity $BaTiO_3$, CeO_2 and $MnCO_3$ fine grained Murata powders. The specimens with and without additives were sintered in air atmosphere at $1370°C$ for three hours. The content of CeO_2 and $MnCO_3$ ranged from 0.10 to 0.45 wt. % and were determined to be the lowest concentration necessary to achieve a nearly uniform microstructure.

SEM microscopy has been used for detailed microstructural examination of sintered specimens. Specimens for electrical properties measurements were prepared in the form of disks with $16.5mm$ diameter and $0.57mm$ high. Capacitance and $\tan\delta$ measurements were conducted on samples coated with silver paste, using Hewlett Packard Instrument 4276 A LCZ Meter. The capacitance was measured at a fixed frequency of 1 kHz.

Hewlett Packard Network Analyzer 8753 C, capable of operation from 300 kHz to 50 MHz and 3 MHz to 6 GHz was used for frequency characteristic measurements.

The hysteresis loops acquisition were performed using the Ferroelectric Tester with SONY/TEKTRONIX336 and Hewlett Packard 7044AX–Y Recorder type plotter.

The polarization at peak voltage and the polarization at zero voltage were measured at 20 and $-10°C$.

3. Results and discussion

In order to better understand the ferroelectric and hysteresis behaviour of barium–titanate ceramics, two parameters which is to beleive to be critical, the grain size and the type of additives, must be taken into account. A significant difference in grain size for barium–titanate without and with additives resulted in different polarization and dielectric constant values. The average grain size in $BaTiO_3$ with ingredients, varied from 6 to $10\mu m$ for sintering temperature of $1370°C$, while the grains, in the barium–titanate compacts sintered without additives, are very large and non uniform, ranged from 20 to $50\mu m$. At higher sintering temperature such as $1370°C$, due to the secondary cristallization, the intensive grain growth occurs, and the coalescence of pores is remarquable one. The microstructure of the undoped barium–titanate clearly reveals the polygonization of grains with many large faulted grains as is shown in Fig. 1.

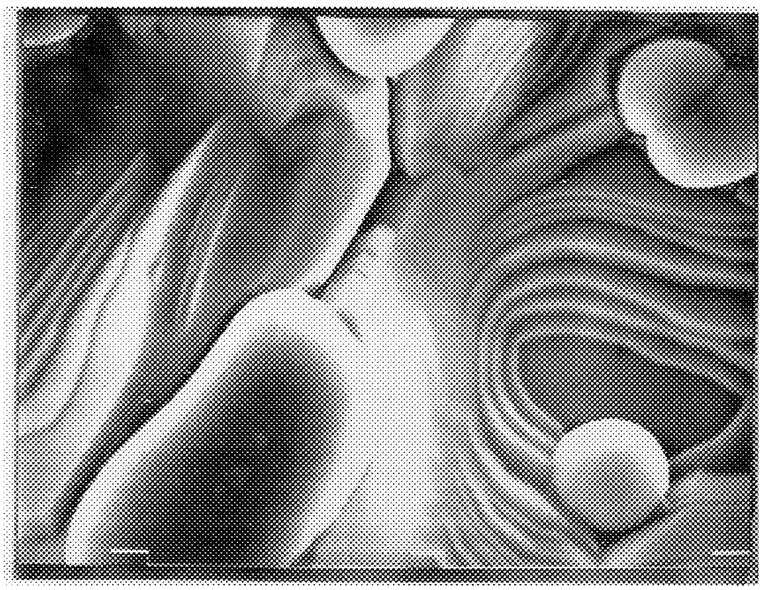

Figure 1. SEM micrograph of $BaTiO_3$ sintered at $1370°C$ for 3 hours ($\times 5000$).

The beneficial effect of CeO_2 is illustrated in Fig. 2 where the fine grained microstructure is the main feature of the doped barium–titanate compacts. The lack of planar defects in doped ceramics compacts could be attributed to the averaging of internal stress over many small grains and pores. It is worth to notice that the majority of small pores are situated at the grain boundaries.

The average grain size together with some electrical parameters is given in Table 1.

Several important features of the data presented in Table 1 should be noticed. Firstly, the polarization values at room temperature consequently increase with the increase of grain size. At low temperature of $T = -10°C$, which indicates that the phase transformation from the tetragonal to the orthorhombic phase has been proceeded, the polarization values are higher as compared to that ones obtained at room temperature.

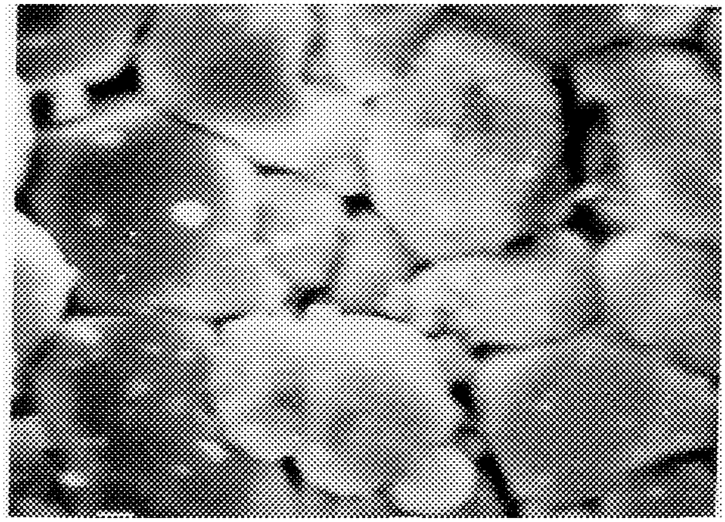

Figure 2. SEM micrograph of $BaTiO_3$ with 0.30 w.t.% CeO_2 sintered at $1370°C$ ($3h$) (×5000).

As it could be seen from Table 1, the polarization values in the orthorhombic state do not differ in a great extent and are almost independent of grain size, however, some discrepancy is noticed only for specimens with 0.30 wt% of CeO_2. The other feature which can be seen from Table 1, is the change of $\tan\delta$ with the grain size and additives concentration. Concerning the values of $\tan\delta$, it is obvious that the resulting compacts with additives, have low value of $\tan\delta$ and consequently low dielectric losses. It is also observed, that with the increase of CeO_2 content, $\tan\delta$ slightly decreases, as well as dielectric constant.

The effect of the appropriate additives on the electrical properties of barium–titanate ceramics was studied by the acquisition of the ferroelectric hysteresis loops. In Fig. 3, the typical hysteresis loops for specimens with 0.30 and 0.45 wt.% CeO_2, have been presenteed. The loops, corresponding to lower concentration of CeO_2, show clearly, for both investigated temperatures, the ferroelectricity behaviour, while for higher concentration of CeO_2, a combination of linearity at room temperature, and ferroelectricity at lower temperature are evident. The complete switching, however, is achieved for voltage ranged from 20 to 60 V.

Table 1. Selected dielectric parameters for specimens sintered at 1370°C for 3 hours.

Type	mean grain size [μm]	ε_r	$P_{20°C}$ [C/m^3]	$P_{-10°C}$ [C/m^3]	$\tan\delta$
none additive	20–50	1621	5813	6702	0.039
Basic mixture 0.10% CeO_2 0.14% $MnCO_3$	6.5	8013	908	5940	0.0081
0.30% CeO_2 0.14% $MnCO_3$	10	7520	959	3135	0.0061
0.45% CeO_2 0.14% $MnCO_3$	9.4	7402	1353	6015	0.0057
0.30% $MnCO_3$ 0.10% CeO_2	6	6871	1722	6188	0.0085
0.45% $MnCO_3$ 0.10% CeO_2	5.9	5724	2403	7425	0.0105

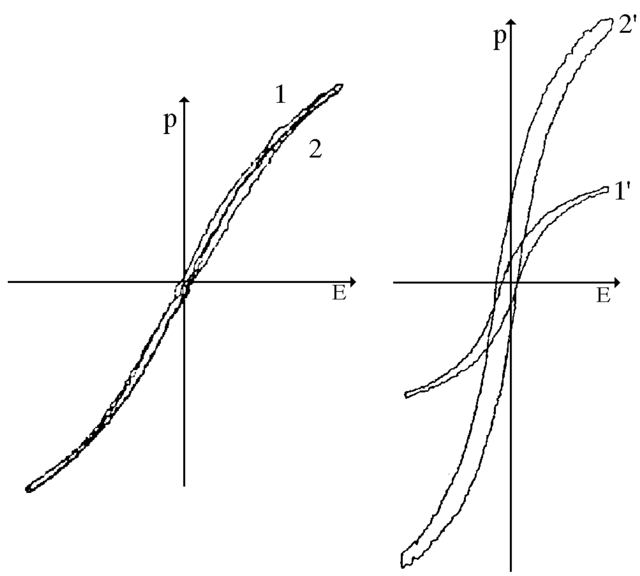

Figure 3. Hysteresis loops in $BaTiO_3$ with 0.30 (1) and 0,45 wt.% (2) CeO_2 at 20°C and with 0.30 (1') and 0.45 (2') CeO_2 at -10°C.

The hysteresis loops, in the sintered specimens with the various content of $MnCO_3$, are similar to that ones obtained for CeO_2 doped ceramics at room temperature and show higher polarization values in the orthorhombic than in the tetragonal state.

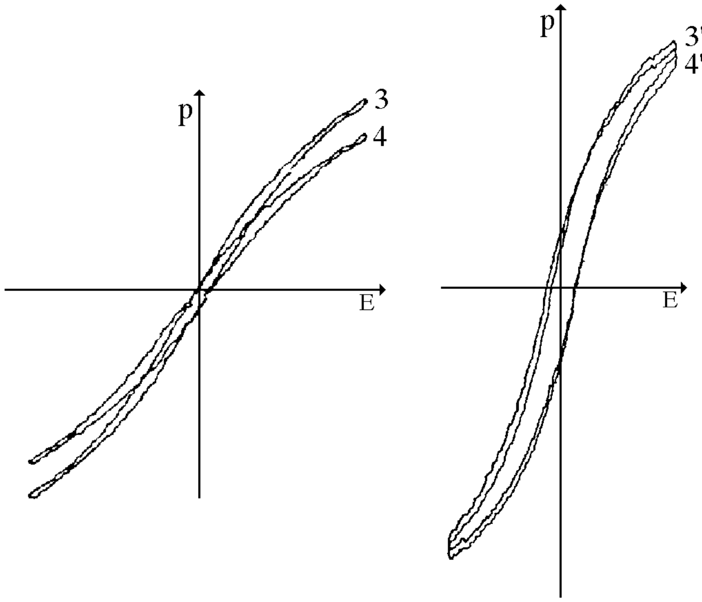

Figure 4. Hysteresis loops of $BaTiO_3$ with 0.30 (3) and 0.45 w.t.% (4) $MnCO_3$ at $20°C$; with 0.30 (3') and 0.45 (4') $MnCO_3$ at $-10°C$.

It could be also pointed out, that the coercitive fields are slightly higher for $MnCO_3$ doped ceramics than that ones with CeO_2. From Fig. 3 and 4. it is evident that the hysteresis losses for doped ceramics are very weak at room temperature as compared to that ones for $T = -10°C$. The difference in hysteresis losses could be attributed to the different cristallographic structure of barium–titanate at $T = 20°C$ and $T = -10°C$.

Apart of these results, it has been shown [9] that the great extent of linearity in hysteresis loops is associated for Fe_2O_3 doped barium–titanate ceramics and consequently the hysteresis losses are smaller, unfortunately the dielectric constant are also smaller. The Curie temperature of barium–titanate ceramics is very sensitive to the dopant concentration and grain size. Although the Curie temperature in $MnCO_2$ and CeO_2 doped ceramics is shifted generally towards the lower temperatures, in specimens with 0.30 wt.% CeO_2 and 0.14 wt.% $MnCO_3$, the Curie temperature is not sharply defined up to $160°C$.

One of the possible reason for smearing out the Curie point and for flatt permittivity response above $35°C$, observed in the present study, can be associated with the existence of core–shell microstructure [5,7]. Apart of this explanation the broadening of the boundaries may be a result of pore pinning. The small grained microstructure with the fine pores situated at the grain boundaries, which is the main characteristic of the obtained compacts, enables the formation of the blocking layers between ferroelectrics region, thus contributing to the temperature stability of dielectric permittivity.

Another interesting feature of the resulting materials, from the point of view of their capacitor applications, is related to the frequency characteristics of doped $BaTiO_3$–ceramics. Along with the large dielectric permittivity and low hysteresis losses, the frequency characteristics of $MnCO_3$ and CeO_2 doped ceramics are improved in a considerable extent. As can be seen from Fig. 5, the frequency region is moved towards the higher frequency values by the increasing the $MnCO_3$ and CeO_2 content in $BaTiO_3$–ceramics.

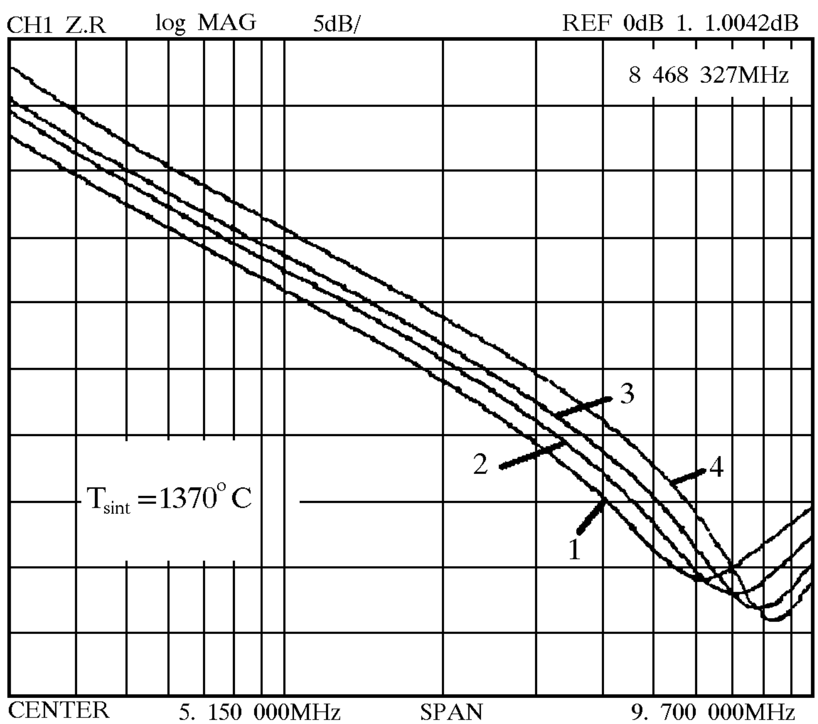

Figure 5. The frequency characteristics of $BaTiO_3$ with various content of CeO_2 $(0.30\% - 1., 0.45\% - 2.)$ and $MnCO_3$ $(0.30\% - 3., 0.45\% - 4.)$.

4. Conclusion

$BaTiO_3$ specimens sintered at $1370°C$ with various content of CeO_2 and $MnCO_3$, demonstrated high permittivity value, a low dielectric and hysteresis losses and can be used as a suitable material for capacitor applications. With the increase of CeO_2 and $MnCO_3$ content, the frequency characteristics are shiftted towards the greater values of frequency, thus improving the capacitor properties of doped ceramic systems. The synergestic effect of CeO_2 and $MnCO_3$ contributed to the small grained microstructure and consequently to the high permittivity values. The flatt permittivity response and broadening of the Curie point up to $160°C$ could be obtained in the system with 0.30 wt.% CeO_2 and 0.14 wt.% of $MnCO_3$.

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