

## MnCO<sub>3</sub> and CaZrO<sub>3</sub> Additive Effects on Electrical Properties of BaTiO<sub>3</sub> Ceramics

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Mn, Ca and Zr as additives have a strong influence on sintering behavior and microstructure evolution of BaTiO<sub>3</sub> which in turn is related to the modifications of permittivity and dissipation factor. In this paper comparative investigations of microstructure and dielectric properties of ceramics doped with 1.5 wt% of MnCO<sub>3</sub> and CaZrO<sub>3</sub> have been done. In order to correlate the green density to the dielectric properties the powders were pressed under different pressing pressure. The pellets were sintered at 1300°C for two hours. Structural characterization has been done by SEM and EDS. Permittivity and dissipation factor have been investigated in function of frequency and temperature dependence of  $\epsilon_r$  has been measured in interval from 20 -200°C. The average grain size was around 1  $\mu\text{m}$  in MnCO<sub>3</sub>/BaTiO<sub>3</sub> compare to 2-3  $\mu\text{m}$  grain size in CaZrO<sub>3</sub>/BaTiO<sub>3</sub> samples. The dielectric constant ranged from 2400 to 1400 being the highest in Mn doped BaTiO<sub>3</sub>. Nevertheless of starting pressure, the frequency characteristics of dielectric constant are similar for both doped samples. Small values of dissipation factor have been detected in both samples being 0.02 and 0.08 for MnCO<sub>3</sub> and CaZrO<sub>3</sub> doped ceramics respectively. The  $\epsilon_r$  (T) became sharp near the phase transition temperature.

Key words: BaTiO<sub>3</sub> ceramics, dielectric constant, dissipation factor, sintering, additive.

### 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<sub>3</sub> 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<sub>3</sub> depend in a great extent on the grain growth during sintering and on additive type and concentration. For the application of doped BaTiO<sub>3</sub> ceramics as a capacitor material, apart from a good density, a high dielectric constant and low loss factor have to be achieved. For a high dielectric constant a uniform microstructure and homogeneous dopants distribution are needed [4], although for semiconducting BaTiO<sub>3</sub> with high PTC effect a bimodal microstructure is preferable.

The 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<sub>x</sub>Ca<sub>1-x</sub>Ti<sub>y</sub>Zr<sub>1-y</sub>O<sub>3</sub> solid solution. The addition of CaO effectively prevents the grain growth [5, 6], improves the electromechanical properties and increases the temperature region where the tetragonal phase is stable, while the ZrO<sub>2</sub> broadens the dielectric peak without affecting a loss factor [7, 8]. However, limited researches have been reported on sintering behavior and electrical properties of CaZrO<sub>3</sub>/BaTiO<sub>3</sub> ceramics. The influence of Mn on the electrical and semiconducting properties of BaTiO<sub>3</sub> has been widely investigated [9,10].

For multilayer capacitors, in attempt to increase the reliability of material, acceptor type dopants such as Mn

can be used to counteract the effect of the oxygen vacancies [10].

For high quality PTC thermistor, it has been reported that Mn is among the most effective acceptor type dopant that segregates along the grain boundaries.

The purpose of this paper was to analyze the electrical properties of BaTiO<sub>3</sub> doped with a small amount of MnCO<sub>3</sub> or CaZrO<sub>3</sub>, previously pressed under different initial pressing pressure. The influence of dopant and different initial pressing pressure on the microstructure, dielectric constant and dielectric losses in function of frequency and temperature has been investigated.

### 2. EXPERIMENTAL

The specimens were prepared starting from commercial "Murata" BaTiO<sub>3</sub>, MnCO<sub>3</sub> and CaZrO<sub>3</sub> powders. The powders were mixed in isopropyl alcohol, dried for several hours before being pressed into pellets under pressing pressure of P = 86, 105 and 120 MPa. The samples doped with 1.5 wt% of MnCO<sub>3</sub> or CaZrO<sub>3</sub> was used for this investigation. The pellets were sintered in air atmosphere in tunnel type furnace at 1300°C for two hours. Microstructural characterization for various samples was carried out using a scanning electron microscope SEM, JEOL-5300 equipped with energy dispersive spectrometer (EDS) system. For electrical measurements silver paste was used on flat surfaces of the specimen. The dielectric properties (dielectric constant and dielectric loss) were measured using HP 4276 LCF meter in frequency range 1-20 kHz. The variation of capacitance with temperature was measured at temperature from 20 to 200°C.

### 3. RESULTS AND DISCUSSION

#### 3.1 Microstructural investigation

The microstructure of BaTiO<sub>3</sub> with 1.5wt% MnCO<sub>3</sub> (compacting pressure of 120 MPa) is shown in Fig. 1.

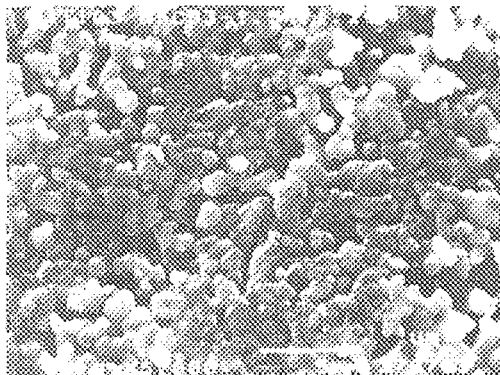


Fig.1 SEM image of MnCO<sub>3</sub> doped BaTiO<sub>3</sub>.

MnCO<sub>3</sub>/BaTiO<sub>3</sub> ceramics exhibits normal grain growth and a fairly uniform microstructure has been observed with average grain size about 1μm. The density of MnCO<sub>3</sub> doped BaTiO<sub>3</sub> 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. A similar microstructures were observed for specimens obtained by two other pressures (86 and 105 MPa).

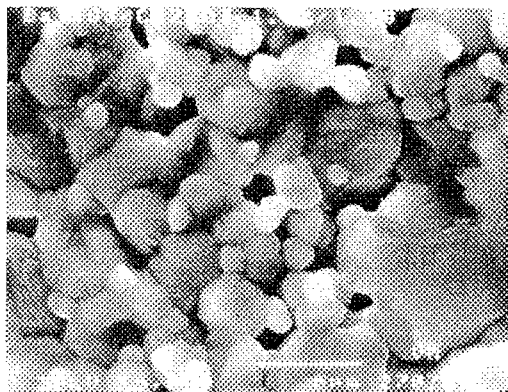


Fig.2 SEM image of CaZrO<sub>3</sub> doped BaTiO<sub>3</sub>.

The average grain size in CaZrO<sub>3</sub> doped BaTiO<sub>3</sub> is around 3μm, although some grains size 5μm are also presented, as can be seen in Fig.2. The sintering density is 70% of theoretical density for samples pressed at 86 MPa and 80% for samples pressed at 120 MPa.

For both types of doped samples, the initial pressing pressure has a small effect on the microstructure development. For higher pressure of 120 MPa, the porosity is reduced and it has been found that the phase composition was not uniform throughout the whole CaZrO<sub>3</sub>/BaTiO<sub>3</sub> surface. According to the EDS analysis, some Ca or Zr rich regions were detected. The additive rich phases are formed in local regions due to inhomogeneous mixing of starting powders.

These phases may be the possible additive source in prolonged time of sintering.

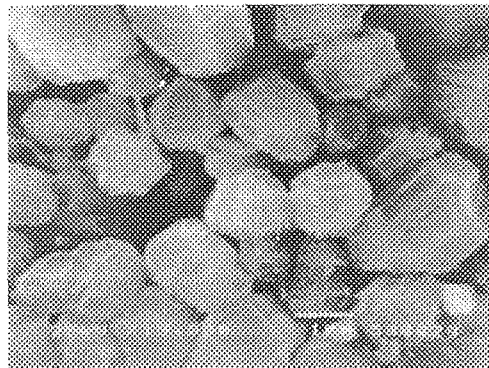


Fig.3 SEM image of etched surface of CaZrO<sub>3</sub>/BaTiO<sub>3</sub>

The etched surfaces of CaZrO<sub>3</sub>/BaTiO<sub>3</sub> show the unusual habit of grain growth as presented in Fig.3. SEM image also reveals that the domain structure is formed within the grains size greater than 1μm.

#### 3.2 Dielectric properties

The dielectric properties evaluation has been done by capacitance and dielectric loss measurements in frequency range from 1-20 kHz. The dielectric permittivity ( $\epsilon_r$ ) in function of frequency for MnCO<sub>3</sub> and CaZrO<sub>3</sub> doped BaTiO<sub>3</sub>, for initial pressing pressure of 86 and 120 MPa, are shown in Fig.4 and 5.

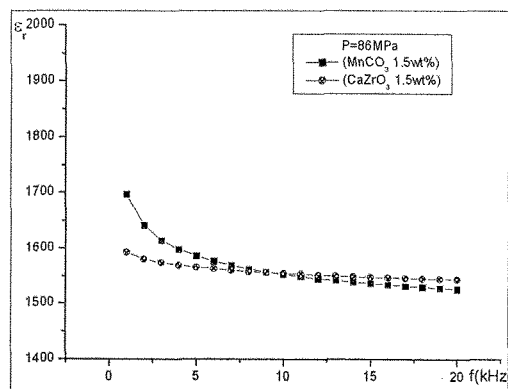


Fig.4 Dielectric constant vs. frequency for MnCO<sub>3</sub> and CaZrO<sub>3</sub>/BaTiO<sub>3</sub> ceramics pressed at 86MPa.

The room dielectric constant ranged from 2200 to 1500 being the greatest in MnCO<sub>3</sub>/BaTiO<sub>3</sub> samples pressed under 120 MPa. For pressure of 120MPa the frequency characteristics of MnCO<sub>3</sub>/BaTiO<sub>3</sub> and CaZrO<sub>3</sub>/BaTiO<sub>3</sub> are similar. Some effect of pressing pressure on the frequency characteristics is observed in MnCO<sub>3</sub>/BaTiO<sub>3</sub> samples. At frequency higher than 5 kHz for both types of samples the permittivity become constant. In CaZrO<sub>3</sub>/BaTiO<sub>3</sub> sample pressed at 120 MPa, where a chemically inhomogeneous system is formed, the overall dielectric behavior is governed by two different microstructural regions, thus leading to the decreasing of dielectric constant compare to the same one in MnCO<sub>3</sub>/BaTiO<sub>3</sub> ceramics (Fig.5).

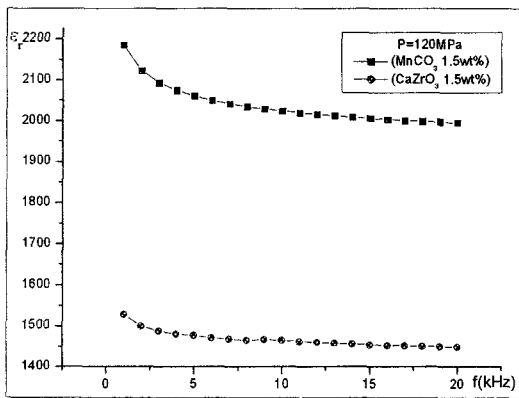


Fig.5 Dielectric constant vs. frequency for MnCO<sub>3</sub> and CaZrO<sub>3</sub> doped BaTiO<sub>3</sub> pressed at 120MPa.

Regarding the dissipation losses (Fig.6 and 7), for all of investigated samples a low values of *tanδ* have been measured, ranged from 0.08 to 0.02. The corresponding *tanδ* - frequency curves for both series of sample could be separated into two regions with a change in linearity at *f*=10 kHz.

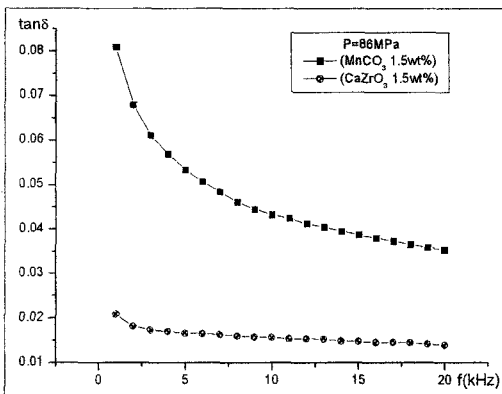


Fig.6 Dielectric loss vs. frequency for MnCO<sub>3</sub> and CaZrO<sub>3</sub> doped BaTiO<sub>3</sub> pressed at 86 MPa.

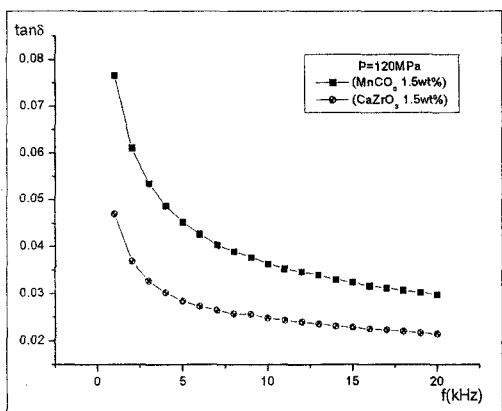


Fig.7 Dielectric loss vs. frequency for MnCO<sub>3</sub> and CaZrO<sub>3</sub> doped BaTiO<sub>3</sub> pressed at 120MPa.

Nearly constant and low value of *tanδ* is noted in CaZrO<sub>3</sub>/BaTiO<sub>3</sub> pressed under 86 MPa, whereas dielectric loss measurements show a similar behavior for CaZrO<sub>3</sub>/BaTiO<sub>3</sub> and MnCO<sub>3</sub>/BaTiO<sub>3</sub> samples obtained

under higher initial pressing pressure (Fig.7).

The contribution of initial pressing pressure and corresponding additives on the dielectric behavior of doped BaTiO<sub>3</sub> can be analyzed through permittivity-temperature curves shown in Fig. 8 and 9.

In general, the permittivity-temperature response and a sharp phase transition, from ferroelectric to paramagnetic phase at Curie temperature, are identical for both types of samples. As presented in Fig.8 and 9, the dielectric constants are affected by initial pressure. Unfortunately, it was not possible to make a strong correlation between initial pressures and permittivity values. For MnCO<sub>3</sub>/BaTiO<sub>3</sub> a high dielectric constant of 7000 is noted for 120 MPa. In CaZrO<sub>3</sub>/BaTiO<sub>3</sub> (Fig.9) ceramics the highest values of dielectric constant, at Curie temperature, correspond to the sample pressed at 105 MPa, being around 7500 compare to 6000 and 5500 in samples pressed under 86 MPa and 120 MPa respectively. Whereas the influence of initial pressure on room temperature dielectric constant was negligible, its influence became significant at higher temperatures.

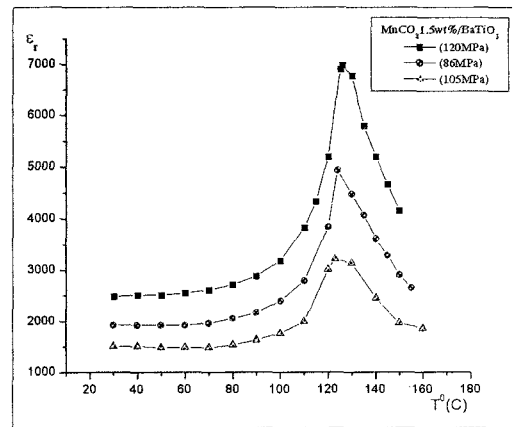


Fig.8 Dielectric constant vs. temperature for MnCO<sub>3</sub>/BaTiO<sub>3</sub>.

It is for believed that above room temperature a relatively large amount of porosity and especially its random distribution have a strong and unpredictable influence on permittivity.

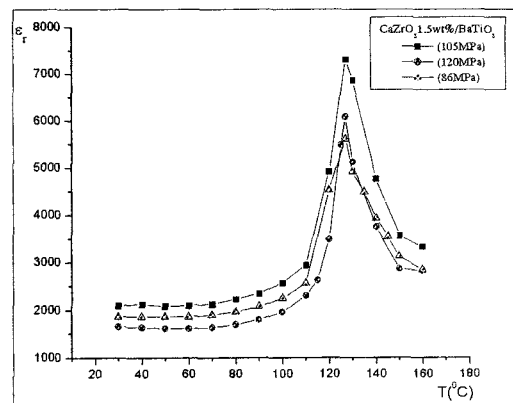


Fig.9 Dielectric constant vs. temperature for CaZrO<sub>3</sub>/BaTiO<sub>3</sub>.

The Curie temperature for all samples (MnCO<sub>3</sub>/BaTiO<sub>3</sub> and CaZrO<sub>3</sub>/BaTiO<sub>3</sub>), nevertheless of starting pressure, is under 120°C.

The Curie-Weiss law can be used to characterize the permittivity behavior above Curie temperature. The 1/ε<sub>r</sub>-temperature curves were fitted and Curie constant for all samples are calculated. The average value of Curie constant for MnCO<sub>3</sub>/BaTiO<sub>3</sub> is 1.70·10<sup>5</sup>K, while for CaZrO<sub>3</sub>/BaTiO<sub>3</sub> is 1.81·10<sup>5</sup>K.

#### 4. CONCLUSION

In this paper comparative investigations of microstructure and dielectric properties of ceramics doped with 1.5 wt% of MnCO<sub>3</sub> or CaZrO<sub>3</sub> and high percentage of porosity have been done. The microstructure and EDS analysis showed that, under the used sintering conditions and because of the inappropriate mixing of starting powders, the sintered samples have a significant amount of porosity and inhomogeneous phase composition. The local regions rich in Mn, Ca or Zr are formed. The initial pressing pressure has no significant effect on the microstructure while a small influence on the phase composition and electrical characteristics has been observed. Among the investigated samples, a greatest value of dielectric constant is detected in MnCO<sub>3</sub>/BaTiO<sub>3</sub>, being 2400, compare to 1400 for CaZrCO<sub>3</sub>/BaTiO<sub>3</sub> at room temperature and 1 kHz. Low values of *tan*δ, ranged from 0.02 to 0.08, have been measured in both series of samples. In general, the permittivity-temperature response and a sharp phase transition at Curie temperature are similar for all investigated specimens.

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