ENHANCED DIELECTRIC PROPERTIES
IN LA MODIFIED BARIUM TITANATE CERAMICS

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Abstract. *Donor/acceptor (La/Mn) doped $BaTiO_3$ ceramics, sintered at different temperatures, were studied regarding their microstructure and dielectric properties as well as the dielectric response in a ferroelectric/paraelectric regime. The concentrations of La^{3+} as donor, ranging from 0.1 to 5.0 at% were used for doping, while a content of Mn^{4+} as acceptor was at 0.05 at% in all samples. The sintering temperature of codoped samples were 1290° and 1350°C.*

A reduction in grain size and fine-grained microstructure with average grain size from 0.5 to 2.0 µm was observed in low doped samples, whereas the abnormal growth of individual grains took place in the 2 at% and 5 at% La doped specimens. The dielectric properties of these samples were investigated as a function of frequency (100Hz – 20 kHz) and temperature (20-180°C). The measured results suggested that both the dielectric constants of the ceramics (ε_r at room temperature and ε_{rmax} at the Curie temperature) decreased as the concentration of La^{3+} increased.

The dielectric permittivity was in the range of 944 to 3200. For samples doped with 0.1 at% La and sintered at 1350°C, the highest dielectric constant value at room temperature (ε_r= 3200) and Curie temperature (ε_r= 5000) were measured. For all measured samples the dissipation factor was less than 0.09. With an increase in La contents, dielectric measurements exhibited shift in the Curie temperature (Tc) towards the low temperature.

Using the Curie-Weiss and the modified Curie-Weiss law, Curie's constant C was calculated as well as the parameter γ, which describes the deviation from the linear dependence ε_r of T above the phase transformation temperature. The calculated values for γ ranged from 1.01 to 1.43. These values indicate a sharp phase transformation in low-doped and diffuse phase transformation in highly La doped samples. The phase transition was reflected in the values of C that started to decrease with increasing dopant content.

Key words: *$BaTiO_3$, dielectric constant, dissipation factor, Curie temperature*

1. INTRODUCTION

Due to its high dielectric constant and low dielectric losses barium titanate is an invaluable electroceramic materials that have been widely used in multilayer ceramic capacitors (MLCCs), temperature sensors, RF filter circuit, electro-optical components and piezoelectric transducer applications [1-3].

In order to be used for MLC applications, barium titanate must be electrical insulators and exhibit high dielectric constant and small dielectric losses at room temperature. As over-current protection devices, temperature sensors and self-regulating heaters they need to be semiconducting, at room temperature and make full use of the PTCR characteristics which are associated with a sharp rise in resistivity when heated above the Curie temperature [4-6].

$BaTiO_3$ is an insulator and a ferroelectric with a tetragonal perovskite structure and a high dielectric constant at room temperature. At the ferroelectric Curie temperature, the crystal structure transforms from tetragonal- ferroelectric to cubic–paraelectric structure. Dielectric properties of $BaTiO_3$-ceramics can be controlled through processing parameters, synthesis method and sintering procedure. Accordingly, it is necessary to prepare homogeneous starting powder, and a ceramics of high density, uniform and fine grain microstructure.

A suitable choice of dopant/additive and careful control of the composition during sintering procedure are one of the most important parameters for modifying the electrical properties of $BaTiO_3$ ceramics [7-12]. Ions with low valence and larger ionic radius (La^{3+}, Ca^{2}) tend to take Ba^{2+} sites, while ions with smaller ionic radii of valence 5^+ and higher (Nb^{5+}) favor the Ti^{4+} sites [13-18]. Incorporation of heterovalent ions in perovskite lattice of barium titanate leads to significant changes of structure and microstructure and furthermore to change of dielectric and electrical properties.

The dielectric characteristics of doped ceramics, in addition to the type and concentration of the additive, are greatly influenced by other parameters such as microstructure, phase homogeneity, pore morphology and domain structure. During the phase transformation of $BaTiO_3$, the domain structure is formed. The configuration and type of domains depends on the development of the microstructure during the sintering process. Homogenous, fine-grained microstructure with monodomain structure allows the obtaining of ceramics of stable ferroelectric characteristics, i.e. ceramics in which the dielectric constant changes slightly with temperature.

During the last few decades, $BaTiO_3$ ceramics, doped with rare earth elements, and especially La, have widely been studied. As a dopant, La is one of the most commonly used materials [19–22]. La^{3+} behaves as a donor as it occupies the Ba site in perovskite lattice. This may raise the dielectric constant and further broaden dielectric peak [23-25]. Also, La as donor decreases the grain size and shifted Curie temperature towards lower values. In La doped samples, the dielectric constant values are much higher than in pure $BaTiO_3$. The partial substitution of Ba^{2+} ions with La^{3+} ions increases the temperature range in which a stable tetragonal phase, characterized by a small change in dielectric constant with temperature. Also, it was found that dielectric losses are reduced by adding La to $BaTiO_3$ [26- 28]

At low concentrations of La (less than 0.5 at %) occurs to the substitution of Ba^{2+} ions and to the formation of solid solutions of the general formula $Ba_{(1-x)}La_xTiO_3$. At higher

concentrations of additives above 1.0 at %, Ba^{2+} or Ti^{4+} ions may be substituted, where the specific electrical resistance of the sample is very high in the order of $10^{10}\,\Omega$cm.

The substitution of La^{3+} on the Ba^{2+} sites requires the formation of negatively charged defects in order to preserve electroneutrality. The charge imbalance can be compensated by three different compensation mechanisms: electrons ($e^{/}$) what constitutes electronic compensation mechanism or barium vacancies ($V_{Ba}^{//}$) and titanium vacancies ($V_{Ti}^{////}$) which represent ionic compensation mechanism [29-32].

For samples sintered in the air atmosphere, the main compensation mechanism is the ionic compensation mechanism, although there is disagreement as to whether this the mechanism takes place through the creation of barium ($V_{Ba}^{//}$) or titanium ($V_{Ti}^{////}$) vacancies. For low partial pressure at low doping levels, the compensation of donors is accomplished by electrons, while for high pressures, the characteristic mechanism is an ionic compensation mechanism.

The influence of MnO_2 on the electrical properties of doped $BaTiO_3$ has been widely investigated [33-35]. In an attempt to increase the reliability of the material, Mn as an acceptor dopant is used to counteract the effects of oxygen vacancies. For PTC thermistor, Mn is among the most effective acceptor type dopant, which segregates along the grain boundaries to enhance the resistance jump at the Curie temperature. Manganese replaces Ti^{4+} ion in $BaTiO_3$ lattice as an acceptor with unstable valence, from Mn^{2+}, Mn^{3+} to Mn^{4+}, depending on the partial pressure of oxygen. In a reducing atmosphere Mn^{2+} is likely to be found but in oxidizing conditions it converts into Mn^{4+}. In air processed samples found both Mn^{2+} and Mn^{4+} with no traces of Mn^{3+}.

The formation of donor acceptor complexes such as $2[La_{Ba}^{\bullet}]\text{-}[Mn_{Ti}^{//}]$ prevents a valence change of Mn^{2+} to Mn^{3+} and has a beneficial effect on reduction of the dissipation factor. Controlled embedding of donor substances, La^{3+}, in combination with the Mn^{2+} acceptor, enables the creation ceramics with a fine grain structure and an increased dielectric constant ε_r, at room temperature and phase transformation temperature compared to $La/BaTiO_3$ ceramics [36-38]. Also, the dielectric losses are lower in the La/Mn codoped ceramics compared to the undoped and La doped ceramics.

In this paper the influence of sintering temperature, donor concentration, acceptor Mn, and their relationship on the performance of ceramics were discussed. Also, the permittivity response with temperature and frequency for specimens doped with various content of La and sintered at different temperatures were analyzed.

2. EXPERIMENTS AND METHODS

The samples of La/Mn doped ceramics used in this investigation were obtained from commercial $BaTiO_3$ powder, ELMIC BT 100 Rhone Poulenc: with a particle size of 0.1μm -0.7 μm. The stoichiometric BaO/TiO_2 ratio was 0.996 ±0.004. La_2O_3 (Merck, Darmstadt) was used as donor dopant. The donor concentration was 0.1 at%-5.0 at%. MnO_2 with a concentration of 0.05 at%, was used as acceptor in all cases. The powders were milled with Al_2O_3 balls in a suspension of ethyl alcohol. The homogenization and milling time was 24h. The powders were then dried at 200°C for several hours and isostatically pressed at 120MPa into cylindrical shaped tablets of 10 mm diameter (Hydraulic Press VPM VEB - Thuringer Industrieverg Raunestein). The prepared tablets

were subjected to the sintering in a laboratory tube furnace (Lenton Thermal Design LTD) at 1290°C and 1350°C in an alumina ceramic boats. The sintering was conducted in air for 2h. The heating mode was 5°C/min to a temperature of 850°C and then of 12°C/min to the desired (sintering) temperature. The cooling rate was 10°C/min to room temperature. The Archimedes' method was used to measure bulk density. A scanning electron microscopy (JSM -5300) equipped with EDS was used to investigate the microstructures of the samples obtained after sintering. The samples were covered with an Au electrodes to improve the conductivity during measurement. The capacitances and the loss tangent of the sintered samples were measured with LCR meter (Agilent 4284A) in the frequency range between 100Hz and 20 kHz. The relative dielectric constant was calculated from the measured capacitance. The temperature interval in which the dielectric constant was measured, is from 20 to 180°C. Curie temperature (T_C), Curie-Weiss temperature (T_0), Curie constant (C) together with critical exponent of nonlinearity (γ) were calculated using modified Curie-Weiss law.

3. MICROSTRUCTURE CHARACTERISTICS

La/Mn -BaTiO$_3$ ceramic density ranged from 72-91% of theoretical density (TD), depending on the sintering temperature and additive concentration. With an increase of the sintering temperature and a decrease of the lanthanum concentration, the density increases while porosity decreases. The smallest density (from 72% TD for 5.0 La/BT to 75% TD for 0.1 La/BT) was measured in samples sintered at 1290°C. The highest density value, 91%TD, has 0.1La/BT sample sintered at 1350°C. The lower densities characteristic for samples doped with higher concentration of La can be due to the formation of a secondary La rich phase, La$_2$Ti$_2$O$_7$ phase, which prevents diffusion during the initial sintering phase.

(a)   (b)
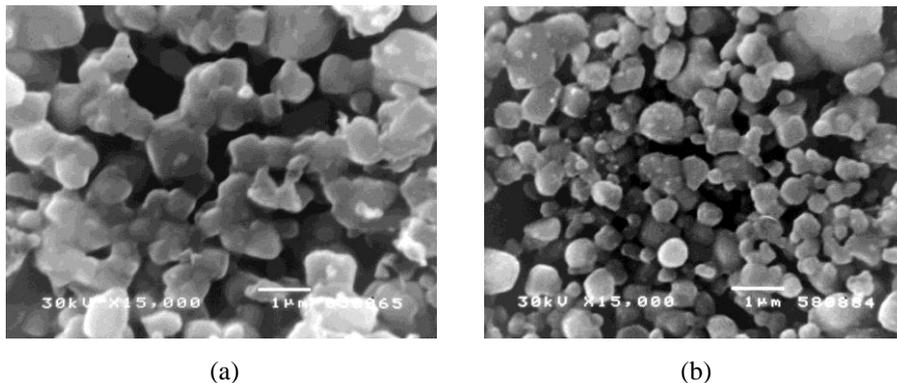
Fig. 1 SEM images of La/Mn doped BaTiO$_3$, sintered at 1290°C
a) 0.1at% La and b) 0.5 at% La.

Fig. 1 shows surface SEM images and grain size distributions of ceramics with 0.1 and 0.5 at% La sintered at 1290°C. It has been found that all low La doped samples have a dense microstructure and uniform grain size. The average grain size of La-doped BaTiO$_3$ ceramics

was from 1.0 to 2.0 μm for La concentrations of 0.1 at%, and 0.5at%. At a sintering temperature of 1350°C, the microstructure of 0.1 and 0.5 at% La doped samples is very similar to the microstructure of the samples sintered at lower sintering temperatures (Fig. 2). The grain size for these samples ranged from 0.5 to 1.5 μm and was characterized by slightly higher density.

(a)   (b)
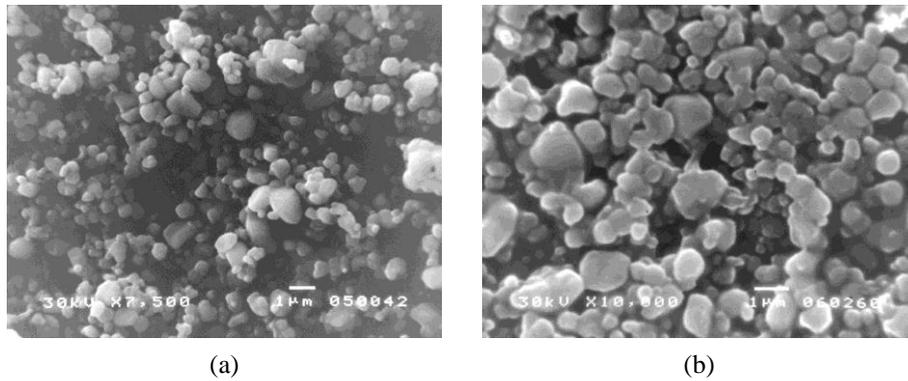
Fig. 2 SEM images of La/Mn doped $BaTiO_3$, sintered at 1350°C
a) 0.1at% La and b) 0.5 at% La.

However, when the La content increased further to 1.0 at%, a slight increase in average grain size was observed. For samples doped with 1.0 at%, 2.0 at% and 5.0 at% La and sintered at 1350°C the microstructure is quite different from the samples sintered at lower temperatures and doped with low additive content. This was related to the formation of individual large grains from 3 to 10 μm as shown in Fig. 3.


(a)   (b)
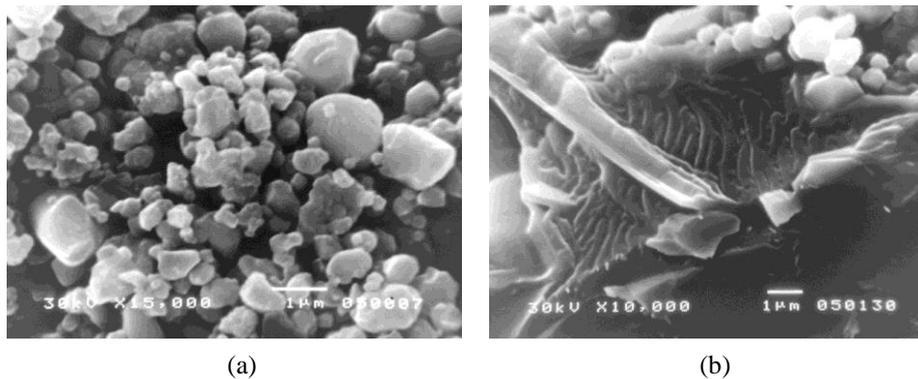
Fig. 3 SEM micrographs of 2.0La/Mn-doped $BaTiO_3$, sintered at 1350°C, a) fine-grained microstructure, b) abnormal growth of individual grains. SEM images were taken from the same sample.

In relation to temperature, the sintering process of La doped $BaTiO_3$ systems can be considered into two different regions, below the eutectic temperature and above the

eutectic temperature. At 1350°C, liquid phase sintering, with a non-homogeneous distribution of the liquid phase, contributes to the abnormal grain growth within the fine-grained structure. One of the specificities of microstructural characteristics, noticed in samples sintered above the eutectic point, is the appearance of the domain structure in individual abnormal grains (Fig 3b).

The pronounced differences in the microstructure are due to the non-homogeneous distribution of La, which can be confirmed by EDS spectra made from different locations on the same sample (Fig. 4).

(a)   (b)
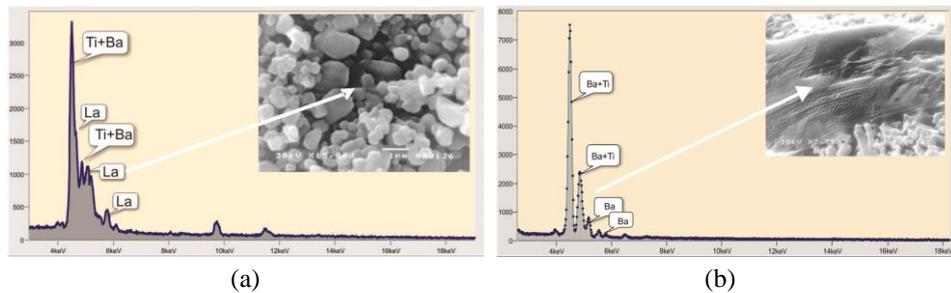
Fig. 4 SEM/EDS images of 2.0 La/Mn doped BaTiO$_3$.a) fine-grained structure rich in La, b) individual large grains with a domain structure.

The presence of La-rich regions indicates two possibilities: first, form a new phase, La$_2$Ti$_2$O$_7$, during the sintering, and the other, La has not been incorporated into the BaTiO$_3$ lattice. XRD analysis shows that the second phase, apart from the BaTiO$_3$ perovskite phase, was not found, which leads to the conclusion that the free La is present in the sample (Fig. 5).The La rich region are associated to the fine-grained microstructure. The EDS spectrum has shown that abnormal grains with a domain structure don't contain La (Fig. 4b). Also, the EDS analysis showed a homogeneous distribution of Mn through the samples, since areas with an increased Mn content were not detected.
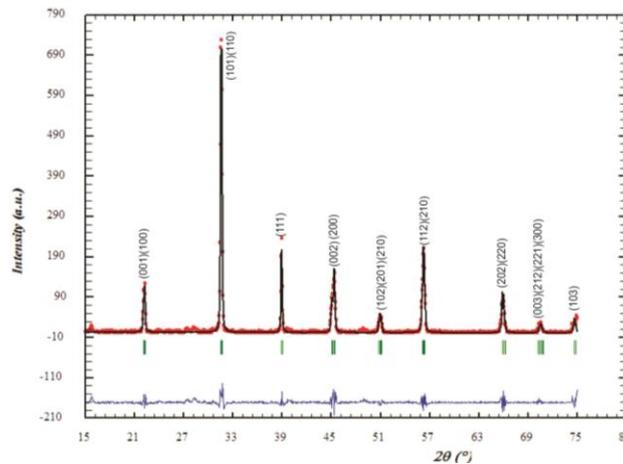

Fig. 5 XRD pattern of the 2.0 at% La-BaTiO$_3$ ceramics. No evidence of any secondary phase.

3. DIELECTRICAL CHARACTERISTICS

The electrical resistivity measurements indicated that all La doped samples behave as electrical insulators and have an electrical resistivity greater than 10^8 Ωcm at room temperature

Dielectric properties, which depend on the microstructural characteristics, type and concentration of additives, were measured as a function of frequency and temperature. The frequency range was from 100Hz to 20 kHz and the temperature range from 20°C to 180°C.

According to the obtained measurement results, as can be seen in Fig.6, the dielectric constant generally decrease with increasing frequency. At high frequencies, dipoles in ceramic materials are incapable of following rapid electric field changes, resulting in limited dipole response which consequently leads to lower dielectric constant. In all La doped samples, after the initial higher value at lower frequencies ε_r decreases its value becomes almost constant for frequencies greater than 3 kHz.
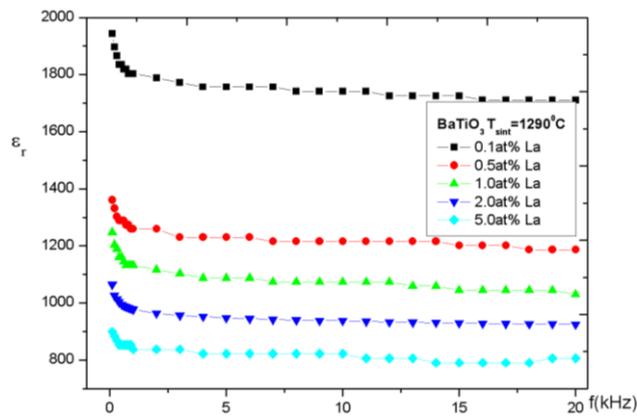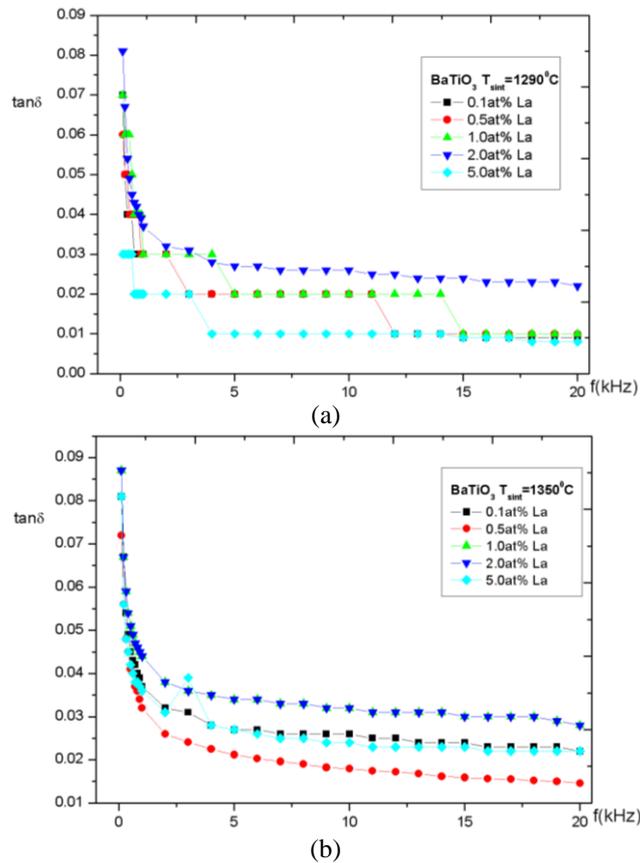

(a)
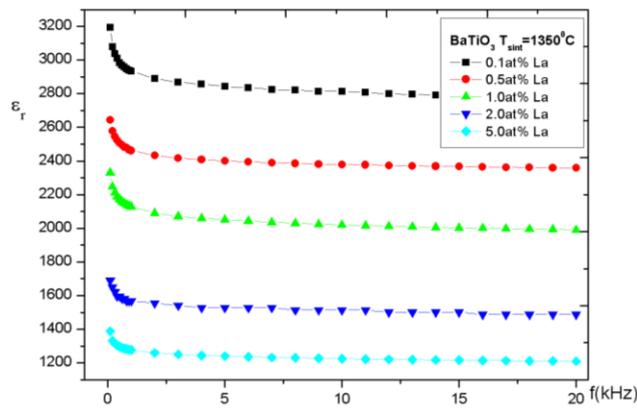
(b)

Fig. 6 Frequency dependence of dielectric constant for La/Mn-BaTiO$_3$ ceramics sintered at a) 1290°C and b) 1350°C.

With an increase of sintering temperature, the porosity of the samples decreases and their density increases, thus increasing the value of the dielectric constant. So the highest values of ε_r have samples sintered at 1350°C. With an increase of additive concentration, the dielectric constant value decreases, so that the maximum value of ε_r was measured for 0.1La/Mn-BaTiO$_3$ samples sintered at 1350°C. The value of the dielectric constant at 100Hz and room temperature ranged from 944 for 5.0La/Mn-BaTiO$_3$ to 1970 for 0.1La/Mn-BaTiO$_3$ ceramics sintered at 1290°C, and from 1450 for 5.0La/Mn-BaTiO$_3$ to 3200 for 0.1La/Mn-BaTiO$_3$ samples sintered at 1350°C.

For all La/Mn-BaTiO$_3$ doped samples are characteristic the low values of the dielectric losses. The highest values of *tanδ* at 100Hz, as well as the largest changes with frequency, from 0.09 to 0.01, were measured for 2.0 and 5.0 at % La doped samples sintered at both sintering temperatures. The main characteristic of the loss tangent for all samples are that after high values at low frequencies, *tanδ* decreases and becomes constant for frequencies above 3 kHz, as shown in Fig.7.


(a)

(b)

Fig. 7 Frequency dependence of dielectric losses for La/Mn-BaTiO$_3$ ceramics sintered at a) 1290°C and b) 1350°C.

The changes of dielectric constant with temperature clearly displays its dependence on the additives concentration and microstructural characteristics.

Among the investigated samples, the highest dielectric constant value at room temperature (ε_r = 3200) and at the Curie temperature (ε_r = 5000), as well as the largest change in the dielectric constant with temperature, shows 0.1La/Mn-BaTiO$_3$ sample sintered at 1350°C characterized by fine grain and uniform microstructure (Fig. 8). For other additive concentrations, the dielectric constant values at Curie's temperature are considerably lower. With an increase of sintering temperature, the values of ε_r are also increased.
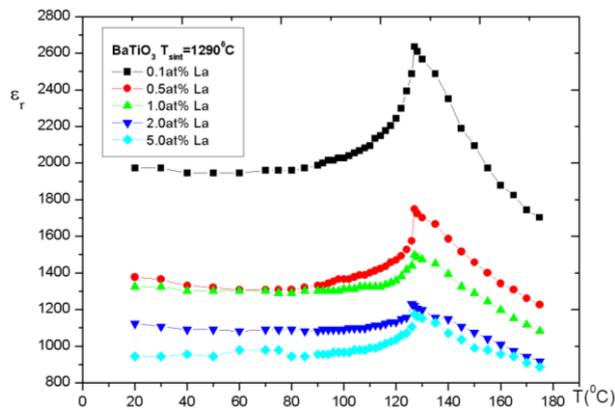
(a)
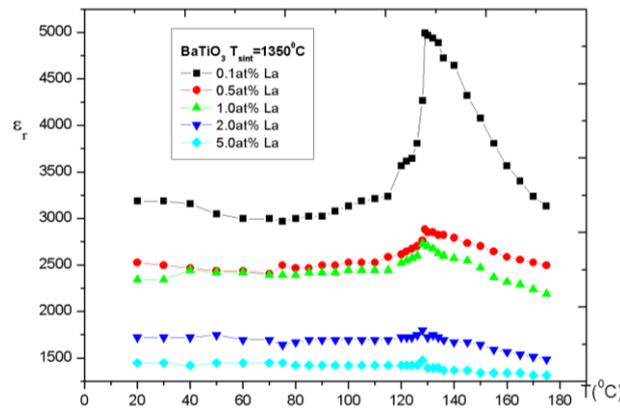
(b)

Fig. 8 Temperature dependence of ε_r for La/Mn-BaTiO$_3$ ceramics.
a) T$_{sin}$=1290°C and b) T$_{sin}$ = 1350°C.

For all the investigated temperatures, it is also characteristic that dielectric constant, decreases with increasing additive concentration. The lowest ε_r value was measured from sample doped with 5.0 at% La and sintered to 1290°C. Lower dielectric constant values in high doped La/ Mn ceramics can be due to lower ceramic density in samples with higher

content of additives or the presence of La-rich regions and the formation of individual large grains which obviously cause a decrease in dielectric permittivity.

In general, the sharp phase transformation from the ferroelectric to the paraelectric phase at Curie temperature was observed in the lower doped (0.1 and 0.5 at% La) $BaTiO_3$ samples. For samples doped with higher La concentration, the nearly flat and stable permittivity response of dielectric constant in the temperature range of 20° to 180°C were observed.

From Fig. 8 it can be seen that the Curie temperature (T_C) was shifted to a higher temperature with the increase of La content. It is because La^{3+} entered Ba site and T_C increased with the incorporation of La^{3+}. The Curie temperature was in the range of 125°C for samples doped with 0.1at% La to 129°C for samples doped with 5.0 at% La (Table 1).
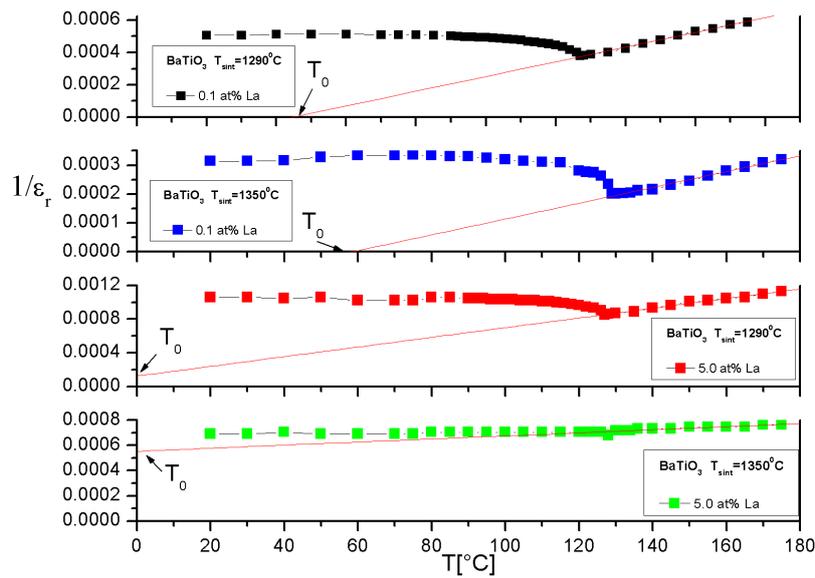

Fig. 9 Reciprocal value of dielectric constant versus temperature for selected La- $BaTiO_3$ samples.

All investigated samples follow the Curie-Weiss law, $\varepsilon_r = C/(T-T_0)$. Based on the Curie-Weiss law, by fitting curves $1/\varepsilon_r$ vs. T, the Curie-Weiss temperature (T_0) and the Curie constant (C) are calculated, for all concentrations and sintering temperatures.

The curves, dependence of the inverse value of the dielectric constant on the temperature for La/Mn-BaTiO$_3$ doped ceramics (Fig. 9), show a linear dependence $1/\varepsilon_r$ vs.T, in the ferroelectric region. Using the linear extrapolation $1/\varepsilon_r$ vs.T is calculated the Curie-Weiss temperature T_0.

The Curie constant was determined by fitting the plot of the reciprocal values of the permittivity in relation to the temperature, and represents the slope of this curve for value above the T_C. Curie's constant value depends largely on the grain size, additive concentration and the porosity of the doped specimens. Since the increase in the additive concentration decreases the density of the samples and increases the grain size, it can be expected that the highest value of

the Curie constant was measured for samples doped with 0.1at% La and sintered at 1350^0C ($C=8.395 \cdot 10^5$K). As the sintering temperature increases, the Curie constant for all sample increases (Fig.10). It has also been observed that the change in the Curie constant with the additive concentration is more pronounced for samples sintered at higher temperatures, where a sharp drop of C is observed for higher additive concentrations. The Curie constant C and the Curie-Weiss temperature T_0 values are given in Table 1.
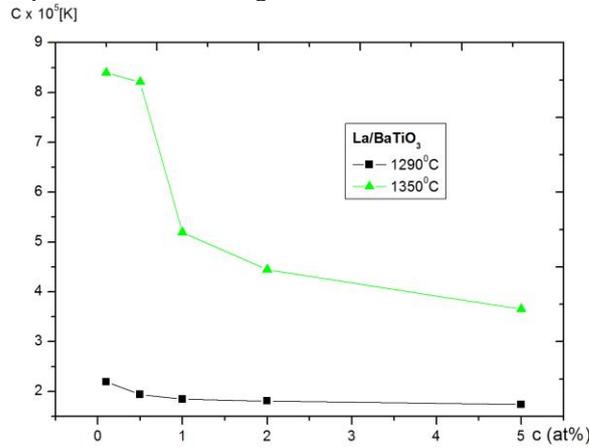
Fig. 10 The dependence of Curie constant on the additive content for doped $BaTiO_3$ samples

The linear fitting of the curves ln $(1/\varepsilon_r - 1/\varepsilon_{max})$ *vs.* ln $(T-Tmax)$, a critical nonlinearity exponent (γ) which represents the slope of the curve was calculated (Fig. 11) [39].
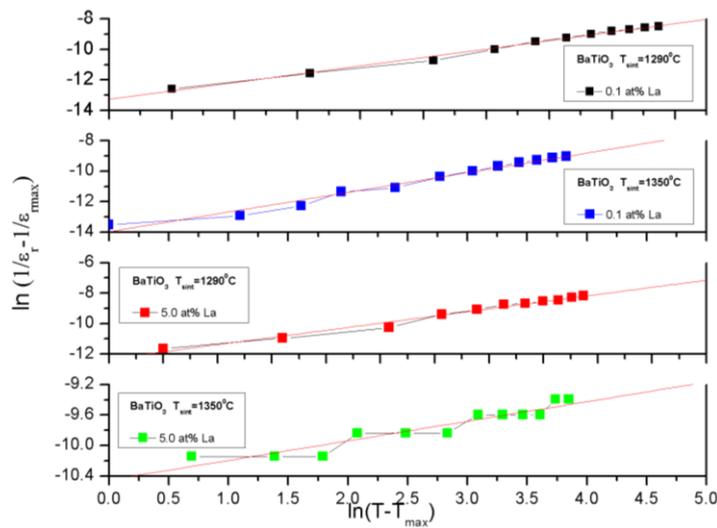
Fig. 11 $ln(1/\varepsilon_r - 1/\varepsilon_{rmax})$ versus ln $(T-T_{max})$ for selected $BaTiO_3$ samples. The critical exponent γ is determined from the slope of curves.

The values of the critical non-linearity exponent (γ) is in the range from 1 to 1.2, for samples with a lower concentration of La and from 1.13 to 1.43 for heavily doped   samples (Fig. 12). The lowest values were observed in samples sintered at 1350°C and doped with 0.1 and 0.5 at% La (γ=1.01) which is in accordance with dielectric characteristics, as these samples show a sharp transition from the ferroelectric to the paraelectric region. For samples sintered at 1290° C these values are higher, especially for samples doped with 2.0 and 5.0 at% La. For these samples, it is characteristic that at the Curie temperature, in addition to structural transformation, there are other processes that are associated with defects at the grain boundary. Also, for these samples, the experimental results showed diffuse phase transformation, which is in agreement with obtained values for γ.
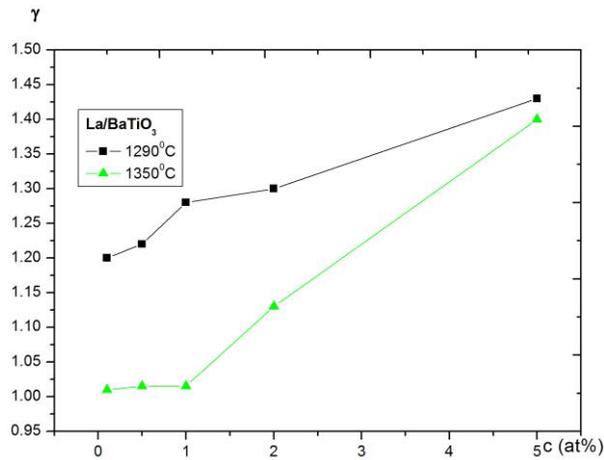
Fig. 12 The critical exponent γ in function of additive content for La doped samples.

Table 1 Dielectric properties for La/Mn doped BaTiO$_3$

La [at%]	$\varepsilon_{r\,max}$	ε_r 300K	$C \cdot 10^5$ [K]	T_C [°C]	T_0 [°C]	$C' \cdot 10^5$ [K]	γ
			T_{sin}=1290^{0}C				
0.1	2630	1970	2.193	126	45	1.68	1.20
0.5	1750	1380	1.938	126	47	1.86	1.22
1.0	1500	1330	1.843	127	6	1.98	1.28
2.0	1230	1150	1.808	127	-20	3.22	1.30
5.0	1175	944	1.738	129	-22	4.04	1.43
			T_{sin}=1350^{0}C				
0.1	5000	3200	8.395	125	58	1.39	1.01
0.5	2880	2530	8.21	126	-122	1.89	1.015
1.0	2750	2350	5.194	127	-65	4.23	1.015
2.0	1800	1730	4.447	128	-165	4.85	1.13
5.0	1430	1450	3.653	128	-455	5.01	1.40

The higher values of the Curie Weiss like constant (C′) have ceramics sintered at 1350° C and they range from $1.39 \cdot 10^5$ K for 0.1 at% La to $5.01 \cdot 10^5$ for 5.0 at% La doped samples. With an increase La concentration, within a single series of samples, the value of C′ increases. The highest values of C′ are calculated for samples doped with 5.0 at% La (Table 1).

4. CONCLUSION

Experimental results revealed that dielectric properties depend on the microstructural characteristics, type and concentration of additives and sintering temperature. The fine-grained microstructure with grains 0.5 - 2.0μm in size were obtained in low doped samples, whereas the abnormal growth of individual grains took place in the higher doped specimens. BaTiO$_3$ ceramics samples doped with 0.1at% La and sintered at 1350°C with a high density and fine grain structure showed the highest values of the dielectric constants at room temperature (ε_r =3200) and at the Curie temperature (ε_{rmax}=5000). For all measured samples the dissipation factor was less than 9%. The Curie-Weiss law characterizes the permittivity of both series of samples and Curie constant is decreasing with an increase of additive content. The highest value of the Curie constant was observed in samples doped with 0.1at% La and sintered at 1350°C (C=8.395·10^5K). The Curie temperature of the doped samples is slightly lower than the Curie's temperature of the undoped ceramics, and it is in the narrow range of 125-129°C. The calculated values for the critical exponent of nonlinearity γ ranged from 1.01 to 1.43 which is in accordance with the measured experimental data and the types of phase transition.

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