

FACTA UNIVERSITATIS

Series: **Electronics and Energetics** Vol. 29, No 2, June 2016, pp. 285 - 296

DOI: 10.2298/FUEE1602285P

DIELECTRIC PROPERTIES OF La/Mn CODOPED BARIUM TITANATE CERAMICS

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Abstract. *La/Mn codoped BaTiO₃ ceramics with various La₂O₃ content, ranging from 0.3 to 1.0 at% La, were investigated regarding their microstructure and dielectric properties. The content of MnO₂ was kept constant at 0.01 at% Mn in all samples. La/Mn codoped and undoped BaTiO₃ were obtained by a modified Pechini method and sintered in air at 1300°C for two hours.*

The homogeneous and completely fine-grained microstructure with average grain size from 0.5 to 1.5 μm was observed in samples doped with 0.3 at% La. In high doped samples, apart from the fine grained matrix, the appearance of local area with secondary abnormal grains was observed.

The dielectric properties were investigated as a function of frequency and temperature. The dielectric permittivity of the doped BaTiO₃ was in the range of 3945 to 12846 and decreased with an increase of the additive content. The highest value for the dielectric constant at room temperature ($\epsilon_r = 12846$) and at the Curie temperature ($\epsilon_r = 17738$) were measured for the 0.3 at% La doped samples. The dissipation factor ranged from 0.07 to 0.62. The Curie constant (C), Curie-Weiss temperature (T_0) and critical exponent (γ) were calculated using the Curie-Weiss and the modified Curie-Weiss law. The highest values of Curie constant ($C = 3.27 \cdot 10^5$ K) was measured in the 1.0 at% La doped samples. The obtained values for γ ranged from 1.04 to 1.5, which pointed out the sharp phase transformation from the ferroelectric to the paraelectric phase.

Key words: Barium titanate, ceramics, dielectrical properties

1. INTRODUCTION

Barium titanate has attracted a considerable amount of attention over the years due to its excellent physical and electrical properties and numerous practical applications [1-3]. The BaTiO₃ based ceramics are widely used for multilayer capacitors (MLCCs), PTC thermistors, varistors, and dynamic random access memories (DRAM) in integrated circuits [4-6]. For MLC applications, dielectric materials need to be electrically insulating and

Received May 8, 2015; received in revised form October 20, 2015

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exhibit high permittivity values and low dielectric losses at room temperature. As overload protection devices, they are required to be semiconducting at room temperature and undergo a sharp rise in resistivity when heated above the ferro- to paraelectric phase transition temperature, T_c [7].

At room temperature, BaTiO₃ adopts a tetragonal perovskite structure and is a ferroelectric with high permittivity. It transforms to the cubic, paraelectric state at the Curie temperature, T_C of 132°C. Also, undoped BaTiO₃ is electrically insulating at room temperature.

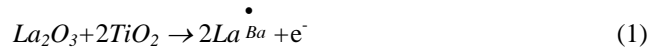
The dielectric properties of BaTiO₃ depend on the synthesis method, density, grain size, and sintering procedure. Consequently, there is a considerable interest in the preparation the powder of high homogeneity and a ceramics of high density and small grain size. The homogeneous starting powders can be obtained by conventional solid state reaction, oxalate precipitation method and modified Pechini process [8, 9]. The Pechini method of preparation has the advantage in raising the permittivity of modified BaTiO₃, compared with the samples obtained by the conventional solid state sintering.

The electrical and dielectric properties of BaTiO₃ ceramics can be modified by using various types of additives, as well as processing procedures [10-12]. Generally, ions with large radius and low valence like La³⁺, Ca²⁺, Dy³⁺ and Y³⁺, tend to enter the A sites (Ba²⁺ sites), while ions with small radius and higher valence like Nb⁵⁺ and Ta⁵⁺ favor the B sites (Ti⁴⁺) [13-17]. Substitution of the barium or titanium ion with small concentrations of ions with a similar radius could lead to structure and microstructure changes, and furthermore, modify the dielectric and ferroelectric properties. Some of the dopants shift transition temperature of BaTiO₃ or induce broadening of ϵ_r - T curve and many of them cause diffuseness of ferroelectric transition. The phase transition from the ferroelectric to the paraelectric phase can be with sharp dielectric maximum or with diffuse dielectric maximum which is characteristic for relaxor ceramics. According to literature data, partial substitution of Ba or Ti ions with dopants such as La, Zn and Sb cause the formation of diffuse phase transition, high dielectric constant and low losses, and Sn, Ce, Zr, Bi, Hf cause the appearance of ferroelectric relaxor behavior [17]. The addition of CaZrO₃ in BaTiO₃ ceramic enhances the capacitance of capacitor and reduces the Curie temperature [18]. Dielectric behavior of Nb⁵⁺ modified BaTiO₃ ceramics was led by the presence of nonferroelectric regions and causes to decrease in the value of dielectric constant. The shift of Curie temperature towards lower temperature side is attributed to the replacement of Ba²⁺ with Bi³⁺ [19]. The addition of Sb affects to the grain growth inhibition and formation uniform microstructure and also to increase the dielectric constant.

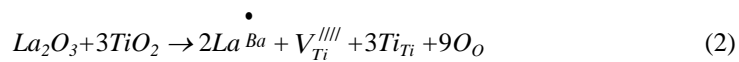
Among the additives, lanthanum, La, is the most efficient in raising the dielectric permittivity of modified BaTiO₃ ceramics [20-22]. La as donor dopant decreases the grain size and enhances the dielectric constant. In La doped ceramics the Curie temperature was shifted towards lower temperatures and dielectric constant values were much higher than in pure BaTiO₃. Also, it was found that the dielectric losses decrease with addition of La in BaTiO₃. At higher concentration of La, dielectric maximum was broadened. The relaxor-type frequency dependence of permittivity was also found in BaTiO₃.

The substitution of La³⁺ on the Ba²⁺ sites requires the formation of negatively charged defects. There are three possible compensation mechanisms: barium vacancies ($V_{Ba}^{//}$), titanium vacancies ($V_{Ti}^{///}$) and electrons (e^{\prime}) [23-25].

Small additions of lanthanum (< 0.5 at%) which replace the Ba ions, leads to the formation of a bimodal microstructure and n-type semiconductivity, which has been widely believed to occur via an electronic compensation mechanism, if the samples are heated in a reducing or argon atmosphere.



In heavily doped samples (> 0.5 at%) sintered in air atmosphere, which are characterized by a small grained microstructure, a high insulation resistance and life stability of the multilayer capacitors can be achieved. The principal doping mechanism is the ionic compensation mechanism (titanium vacancy compensation mechanism).



For low partial pressure of oxygen, the characterized mechanism is electronic compensation mechanism, while for high pressures it is the characteristic ionic compensation mechanism.

MnO₂ are frequently added to BaTiO₃, together with other additives, in order to reduce the dissipation factor. Manganese has double role, as acceptor dopant incorporated at Ti⁴⁺ sites, it can be used to counteract the effect of the oxygen vacancies donors. As additive, segregating at grain boundaries, can prevent the exaggerated grain growth. Manganese belongs to the valence unstable acceptor-type dopant, which may take different valence states, Mn²⁺, Mn³⁺ or even Mn⁴⁺ during post sintering annealing process. Mn²⁺ is stable in cubic phase and easily oxidized to Mn³⁺ state which is more stable in tetragonal phase. For codoped systems [26-28], the formation of donor-acceptor complexes such as 2[La_{Ba}[•]]-[Mn_{Ti}^{///}] prevent a valence change from Mn²⁺ to Mn³⁺.

Generally, in codoped BaTiO₃ ceramics, the controlled incorporation of donor dopant, such as La, in combination with an acceptor (Mn) leads to the formation ceramics with uniform microstructure and high dielectric constant at room temperature as well as at Curie temperature. The codoped ceramic showed lower value of dielectric losses compared to the undoped ceramics. Also, one of the reasons they used a modified BaTiO₃ is that the additives have the effect of moving the Curie temperature in the temperature field that can be used effectively, significantly below 132°C.

The purpose of this paper is to study the dielectric properties of La/Mn codoped BaTiO₃ ceramics, obtain by Pechini method, as a function of different dopant concentrations. The Curie-Weiss and modified Curie-Weiss law were used to clarify the influence of dopant on the dielectric properties of BaTiO₃.

2. EXPERIMENTS AND METHODS

The La/Mn codoped BaTiO₃ ceramics were prepared from organometallic complex based on the modified Pechini procedure [9] starting from barium and titanium citrates. This method provides a low-temperature powder synthesis process (below 800°C), good stoichiometry and easy incorporation of dopants in the crystal lattice. The content of additive oxides, La₂O₃, ranged from 0.3 to 1.0 at%. The content of MnO₂ was kept constant at 0.01 at% in all samples. For comparison purposes the samples free of La and Mn were prepared in the same manner. The modified Pechini process was carried out as a three stage process

for the preparation of a polymeric precursor resin. Solutions of titanium citrate and barium citrate were mixed, heated at 90°C and then the La and Mn were added. The temperature was raised to 120–140°C, to promote polymerization and remove the solvents. The decomposition of most of the organic carbon residue was performed in an oven at 250°C for 1 h and then at 300°C for 4 h. Thermal treatment of the obtained precursor was performed at 500°C for 4 h, 700°C for 4 h and 800°C for 2 h. After drying at room temperature and passing through sieve, the barium titanate powder was obtained. The powders were isostatically pressed at 98 MPa into disk of 10 mm in diameter and 2 mm of thickness. The samples were sintered in air atmosphere at 1300°C for 2 h and the heating rate was 10°C /min. The bulk density was measured by the Archimedes method. The specimens are denoted such as 0.3 La/Mn-BaTiO₃ for specimen with 0.3 at% La and 0.01 at% Mn and so on.

The microstructures of the sintered or chemically etched samples were observed by scanning electron microscope JEOL-JSM 5300 equipped with EDS (QX 2000S) system. Capacitance and dissipation factor was measured using an Agilent 4284A precision LCR meter in the frequency range from 20Hz to 1 MHz. The variation of the dielectric permittivity with temperature was measured in the temperature interval from 20° to 180°C. The dielectric parameters such as Curie-Weiss temperature (T_0), Curie constant (C) and critical exponent γ were calculated according to Curie-Weiss and modified Curie-Weiss law.

3. MICROSTRUCTURE CHARACTERISTICS

The relative density of the La/Mn codoped samples varied from 90% to 95 % of theoretical density (TD), depending on the amount of additives, being lower for higher dopant additive concentration.

The main characteristic of the low doped samples, the samples doped with 0.3at% of La is a completely fine grained and homogeneous microstructure with fairly narrow size distribution. The grain sizes were ranged from 0.5 to 1.5 μm (Fig.1a) and no evidence of any secondary abnormal grain growth. With an increase of the additive content, the microstructure of the specimens doped with 0.5 at% of La showed quite significant grain growth with varied grain size. Besides a small amount of 1 μm grains, most of the grains were approximately 3-8 μm (Fig.1b).

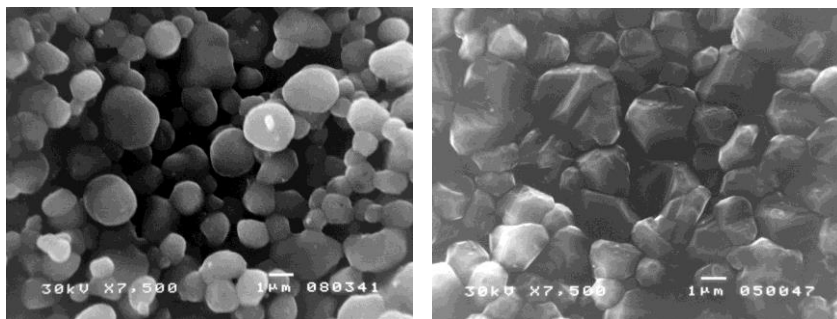


Fig. 1 SEM images of La/Mn codoped BaTiO₃, a) 0.3at% La and b) 0.5 at% La.

The microstructure evolution in the samples doped with 1.0 at% of La was quite different from that observed in the other samples. In 1.0 at% La doped samples, apart from the fine grained matrix with grain size of 2-3 μm , some local area with secondary abnormal grains (Fig.2a) were observed. The secondary abnormal grains size was in the range 10-15 μm .

For undoped BaTiO_3 ceramics, (Fig. 2b) the microstructure displayed the characteristic non-uniform microstructure and grain size distribution from 1-15 μm .

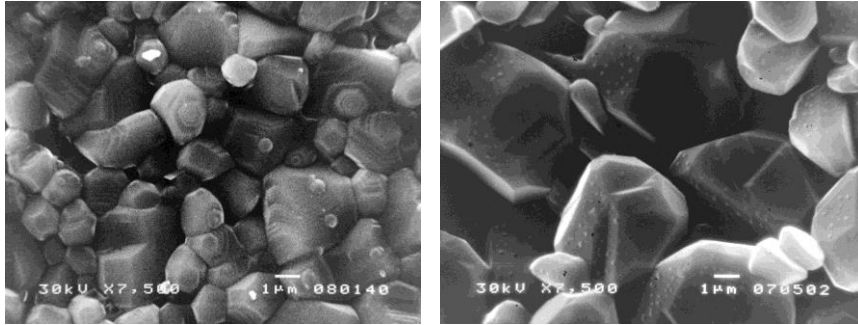


Fig. 2 SEM images of a) 1.0 at% La/Mn codoped BaTiO_3 and b) undoped BaTiO_3 ceramics.

The difference in microstructural features is also associated with the inhomogeneous distribution of La as can be seen in the EDS spectra taken from different areas in the same sample (Fig. 3). The existence of X-ray peaks for lanthanum (L_{α} -La peak) in the 1.0 at% doped sample in EDS spectrum indicates that La-rich regions are in coexistence with the nominal perovskite phase. It is worth noting that the concentrations less than 1.0 at% could not be detected by the EDS attached to the SEM, unless an inhomogeneous distribution or segregation of the additive was present. The La-rich regions are associated with the small grained microstructure, whereas EDS spectrum free of La-content corresponds to the abnormal grains. Also, the EDS analysis did not reveal any content of Mn, thus a homogeneous distribution of Mn through the specimens can be assumed.

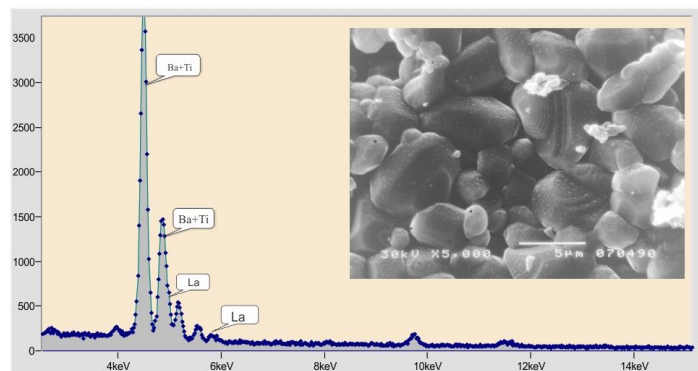


Fig. 3 SEM/EDS images of 1.0 La/Mn codoped BaTiO_3 .

3. DIELECTRICAL CHARACTERISTICS

All La/Mn doped samples that were investigated are electrical insulators with an electrical resistivity $\rho > 10^8 \Omega\text{cm}$ at room temperature. The high resistivity indicates that the ionic compensation mechanism (titanium vacancy compensation mechanism) is exclusively involved during the La incorporation into the BaTiO_3 matrix, and due to the immobility of cation vacancies, at room temperature, the doped samples remain insulating.

The observed microstructural characteristics, which depend on the type and concentration of additive, have a direct influence on the dielectric properties.

Dielectric properties of BaTiO_3 ceramics (dielectric permittivity ϵ_r and dissipation factor $\tan\delta$) were measured as a function of frequency and temperature. Dielectric constant was determined in the frequency range from 20 Hz to 1 MHz. After the initial high value at low frequency, dielectric constant becomes nearly constant at frequency greater than 10 kHz. With an increase of additive content, the dielectric constant decreases. The highest value of the dielectric constant ($\epsilon_r = 12846$) was measured for samples doped with 0.3 at% of La characterized by small-grained microstructure and high sintering density (Fig. 4). The lowest value of dielectric constant ($\epsilon_r = 5200$) was measured for 1.0 at% La doped samples. For the undoped BaTiO_3 ceramic, the dielectric constant was 2230 and for these samples dielectric constant was essentially independent of frequency.

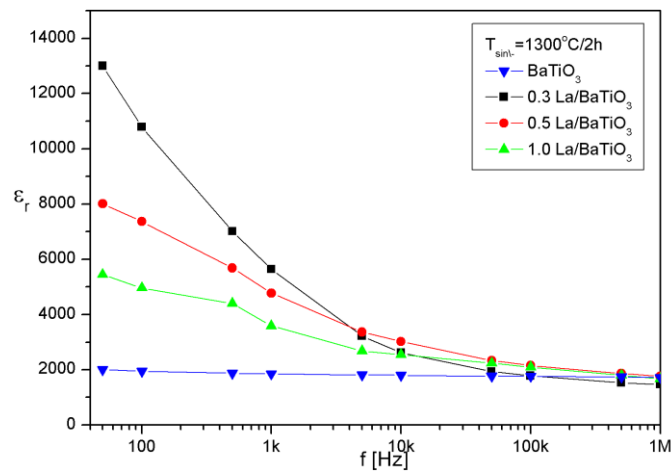


Fig. 4 Dielectric constant of undoped and La/Mn- BaTiO_3 ceramics as a function of frequency.

The dielectric loss ($\tan\delta$) values are in a wide range from 0.07 to 0.62 (Fig 5). The main characteristics for all doped specimens are that after the initial high dielectric loss values, the $\tan\delta$ decreases and are nearly independent of frequency greater than 20 kHz. The highest value of $\tan\delta$, and a considerable change of $\tan\delta$ vs. frequency from 0.61 to 0.2 were recorded in 0.3La/Mn doped BaTiO_3 ceramics.

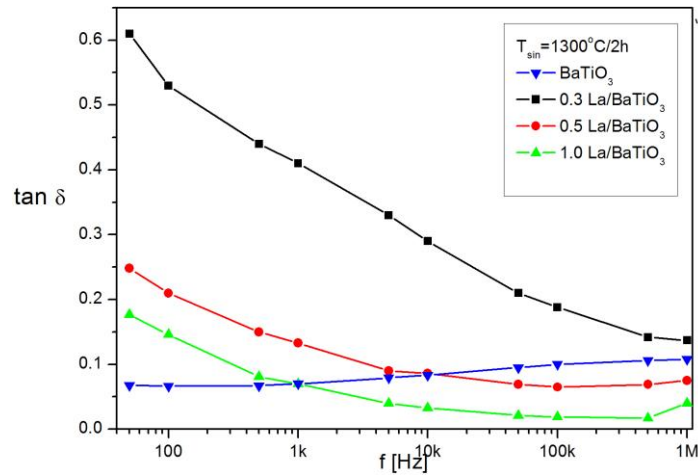


Fig. 5 The dielectric losses as a function of frequency for undoped and La/Mn-BaTiO₃ ceramics.

The dielectric properties of BaTiO₃ ceramics also can be analyzed through the permittivity-temperature dependence (Fig. 6). The variation of the dielectric constant as a function of temperature clearly displays the effects of additive content and microstructural composition on dielectric properties.

The highest value of the dielectric constant at room temperature ($\epsilon_r = 12846$) and at Curie temperature ($\epsilon_r = 17738$), was measured for the 0.3La/Mn codoped BaTiO₃ samples, which is characterized also by a small grained and uniform microstructure and high density.

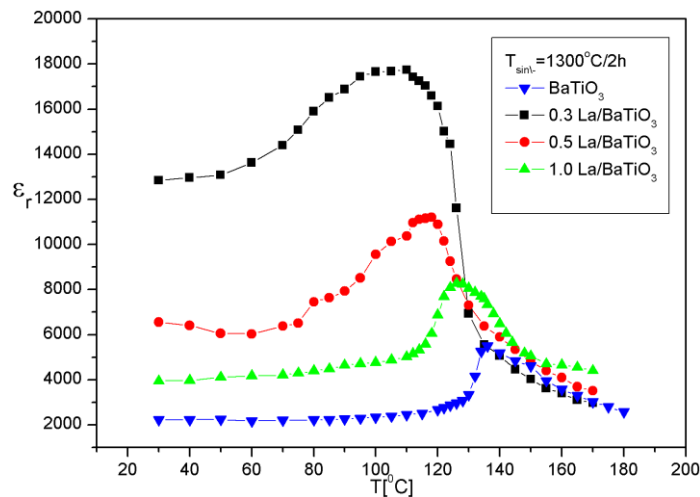


Fig. 6 Dielectric constant of BaTiO₃ ceramics as a function of temperature.

With an increase of additive content the dielectric constant decreases. For the samples doped with 1.0 at% La, the dielectric constant at room temperature is 3945 and at Curie temperature is 8270.

The variations in dielectric constant in low and heavily codoped La/Mn ceramics, sintered at the same temperature, can be attributed on one hand to the different density (where density decreases with an increase of additive content); and on the other hand, to the presence of a La-rich phase and formation of secondary abnormal grains that obviously lead to a decrease in the dielectric permittivity.

In general, the pronounced permittivity-temperature response and a sharp phase transition, from ferroelectric to paraelectric phase at Curie temperature, are observed for all doped BaTiO₃ samples and for undoped BaTiO₃. It can be seen from the ratio of permittivity at Curie point (ϵ_{rmax}) and room temperature (ϵ_{rmin}) i.e. ($\epsilon_{rmax}/\epsilon_{rmin}$) which for 0.3 at% doped samples has a value of 1.38, for the 0.5La/Mn doped samples is 1.7, and for the 1.0 at% doped BaTiO₃ is 2.09.

The Curie temperature (T_c) for codoped samples is shifted towards low temperature compared to undoped BaTiO₃ ceramics for which the Curie temperature is 134°C. For doped samples, the T_c ranged from 110°C for 0.3La/Mn BaTiO₃ to 122°C for 1.0La/Mn BaTiO₃ ceramics (Table 1).

The shift of Curie temperature for the codoped ceramics was heavily dependent on the ratio donor/acceptor. In the 0.3La/Mn-BaTiO₃ ceramics, the donor/acceptor ratio is 30, and in 1.0La/Mn is 100. With increasing La concentrations and the formation of donor-acceptor complexes $2[La_{Ba}^{\bullet}]-[Mn_{Ti}^{//}]$, the possibility of oxidation Mn^{2+} to Mn^{3+} and Mn^{4+} state was reduced. So the influence of Mn on the shift in Curie temperature in 1.0La/Mn BaTiO₃ ceramics was smaller.

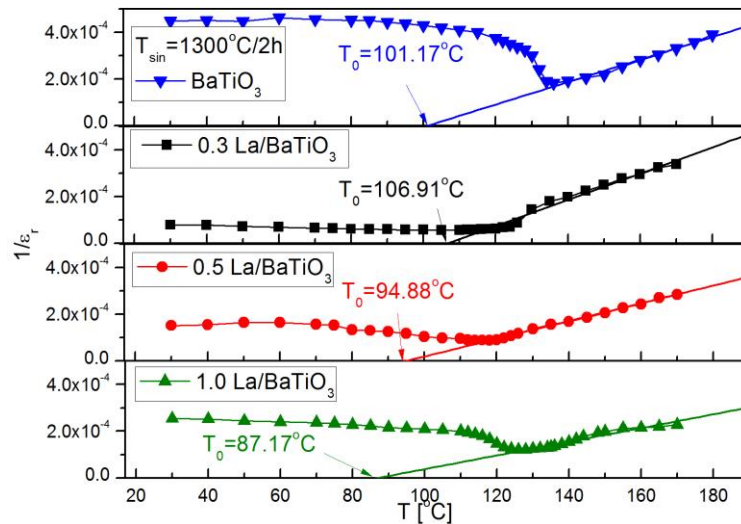


Fig. 7 Reciprocal value of ϵ_r in function of temperature.

All specimens have a sharp phase transition and follow the Curie-Weiss law:

$$\varepsilon_r = \frac{C}{T - T_0} \quad (3)$$

where C is the Curie constant and T_0 Curie-Weiss temperature, which is close to the Curie temperature. The Curie-Weiss temperature (T_0) was obtained from the linear extrapolation of the inverse dielectric constant of temperature above T_C down to zero (Fig. 7). The Curie-Weiss temperature decreased with an increase of additive concentration.

The Curie constant (C) was obtained by fitting the plot of the inverse values of the dielectric constant vs. temperature, and represents the slope of this curve for data above the T_C . With an increase of dopant amount, the Curie constant (C) increased. The highest value of C ($C = 3.27 \cdot 10^5 \text{K}$) was measured for the 1.0 at% La doped samples. The value of the Curie constant is related to the grain size and porosity of the samples. The Curie constant for undoped BaTiO_3 ceramic is ($C = 2.12 \cdot 10^5 \text{K}$). The Curie constant and the Curie-Weiss temperature values are given in Table 1.

In order to investigate the Curie-Weiss behavior, the modified Curie-Weiss law was used [29]

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{r\max}} = \frac{(T - T_{\max})^\gamma}{C'} \quad (4)$$

where ε_r is dielectric constant, $\varepsilon_{r\max}$ maximum value of dielectric constant, T_{\max} temperature where the dielectric value has its maximum, γ critical exponent for diffuse phase transformation (DPT) and C' the Curie-Weiss-like constant. The dielectric parameters for undoped and doped BaTiO_3 ceramics, together with the values calculated according to modified Curie-Weiss law, are given in Table 1.

Table 1 Dielectric parameters for undoped and La/Mn codoped BaTiO_3

Samples	ε_r at 300K	ε_r at T_c	$\tan \delta$ at (300K)	T_c [$^{\circ}\text{C}$]	T_0 [$^{\circ}\text{C}$]	C [K] $\cdot 10^5$	γ
pure BaTiO_3	2230	5488	0.067	134	101.1	2.12	1.402
0.3La/ BaTiO_3	12846	17738	0.610	110	106.9	1.95	1.509
0.5La/ BaTiO_3	6550	11196	0.248	118	94.8	2.67	1.044
1.0La/ BaTiO_3	3945	8270	0.177	122	87.1	3.27	1.536

The critical exponent of the nonlinearity γ was calculated from the best fit of the curve $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ vs. $\ln(T - T_m)$, as shown in Fig. 8. The critical exponent γ represents the slope of the curve. For a single BaTiO_3 crystal, the γ is 1.08 and gradually increases up to 2 for diffuse phase transformation in doped BaTiO_3 .

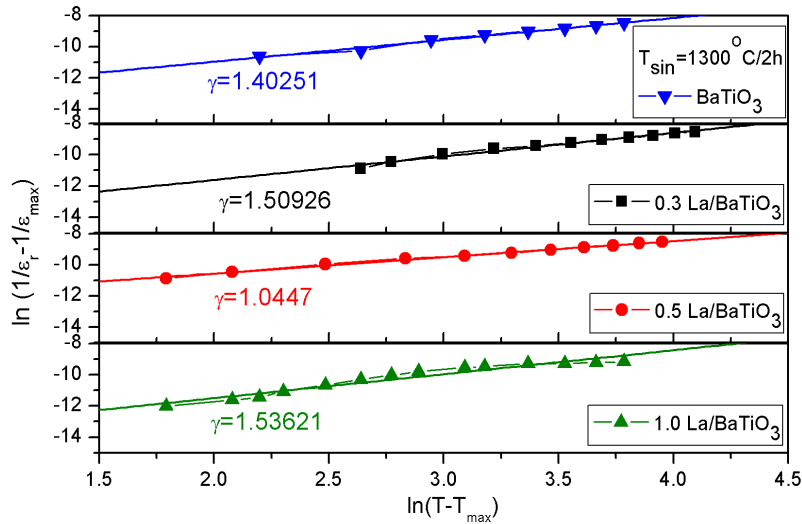


Fig. 8 The modified Curie-Weiss plot $\ln(1/\epsilon_r - 1/\epsilon_m)$ vs. $\ln(T - T_m)$ for BaTiO_3 samples. The slope of the curve determines the critical exponent γ .

As can be shown in Fig.8, the critical exponent γ value is in the range from 1.044 to 1.536, which is in agreement with the experimental data. These samples are characterized by a sharp phase transition from ferroelectric to paraelectric phase at the Curie point. The highest value for the critical exponent γ ($\gamma = 1.536$) was calculated in the 1.0 at% La/Mn doped samples.

4. CONCLUSION

The dielectric properties of La/Mn codoped ceramics depends heavily on the additive concentration and obtained microstructure during sintering. All samples have a resistivity of $\rho > 10^8 \Omega \cdot \text{cm}$ and they are electrical insulators at room temperature. The highest value of the dielectric constant was achieved at room temperature ($\epsilon_r = 12846$) and at the Curie temperature ($\epsilon_r = 17738$), and these values were measured for the 0.3 at% La/Mn doped ceramics. This composition displayed a high density and small grained microstructure. With an increase of the additive content, the dielectric constant decreased; for the samples doped with 1.0 at% La, the ϵ_r is 3945. The differences in dielectric constant values in low and heavily doped BaTiO_3 are due first to the different density (porosity) of doped ceramics and secondly to the presence of non-ferroelectric La rich regions and secondary abnormal grains. The dielectric loss values are in a wide range from 0.07 to 0.62. After initially greater dielectric loss values at low frequency, the $\tan \delta$ decreases and are nearly independent of frequency greater than 20 kHz. All specimens followed a Curie-Weiss law with sharp phase transition. The Curie temperature of doped BaTiO_3 ceramics was shifted towards low temperature compared to undoped BaTiO_3 . The Curie temperature values ranged from 110°C for 0.3La/Mn BaTiO_3 to 122°C for 1.0La/Mn BaTiO_3 ceramics. The Curie constant

increases with increase of additive content. The highest value of C ($C = 3.27 \cdot 10^5 \text{K}$) was measured in samples doped with 1.0 at% of La. The critical exponent γ is in the range from 1.044 to 1.536 and pointed out the sharp phase transformation from ferroelectric to paraelectric phase at Curie temperature.

Acknowledgement: *This research is a part of the Project "Directed synthesis, structure and properties of multifunctional materials" (172057). The authors gratefully acknowledge the financial support of Serbian Ministry of Education, Science and Technological Development for this work.*

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