Microstructure evolution and phase transition in La/Mn doped barium titanate ceramics[#]

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Abstract

La/Mn codoped $BaTiO_3$ with different La_2O_3 content, ranging from 0.1 to 5.0 at% La, was investigated regarding their microstructural and dielectric characteristics. The content of 0.05 at% Mn was constant in all investigated samples. The samples were sintered at 1320°C and 1350°C for two hours. Microstructural studies were done using SEM and EDS analysis. The fine-grained microstructure was obtained even for low content of La. The appearance of secondary abnormal grains with serrated features along grain boundaries was observed in 1.0 at% La-$BaTiO_3$ sintered at 1350°C. Nearly flat permittivity-temperature response was obtained in specimens with 2.0 and 5.0 at% La. Using the modified Curie-Weiss law a critical exponent γ and C'were calculated. The obtained values of γ pointed out the diffuse phase transformation in heavily doped $BaTiO_3$ and great departure from the Curie-Weiss law for low doped ceramics.

Keywords: *$BaTiO_3$, sintering, microstructures, ferroelectric properties*

I. Introduction

Among the modified $BaTiO_3$ compositions, La and La/Mn codoped $BaTiO_3$ ceramics are intensively studied because their attractive dielectric response can be used in various electronic devices. The incorporation of La^{3+}, which replaces A sites in perovskite $BaTiO_3$ structure, modifies the microstructural and electrical properties of doped $BaTiO_3$. For lower donor concentration, up to 0.50 mol% La, named as grain growth inhibition threshold (GGIT), the bimodal microstructure is formed and anomalous grain growth occurred which leads to the semiconductive properties of ceramics [1–6]. The substitution of La^{3+} on Ba^{2+} 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'). For samples sintered in air atmosphere, which are the electrical insulators, the principal doping mechanism is the ionic compensation mechanism. The controversy remains concerning whether the dominate ionic mechanism is through the creation of barium or titanium vacancies [7,8].

In heavily, single La-doped or donor-acceptor La/Mn-codoped $BaTiO_3$ ceramics, with small grained microstructure, the resistivity is in the order of 10^{10} Ωm. MnO or MnO_2 are frequently added to $BaTiO_3$ together with other additives in order to reduce the dissipation factor. Manganese belongs to the valence unstable acceptor-type dopants which may take different valence states, Mn^{2+}, Mn^{3+} or even Mn^{4+} during post sintering annealing process. For codoped systems [9] the formation of donor-acceptor complexes such as $2[La_{Ba}^{\bullet}]$-$[Mn_{Ti}^{//}]$ prevent a valence change of Mn^{2+} to Mn^{3+}.

However, in addition to the various function of additives, it has been pointed out that the formation of liquid phase and secondary phases above the eutectic temperature (1332°C) as well as the Ba/Ti atomic ratio, may also influence the microstructural evolution and ferroelectric properties [10–12].

The purpose of this paper is a comparative investigation of the microstructure and dielectric properties of

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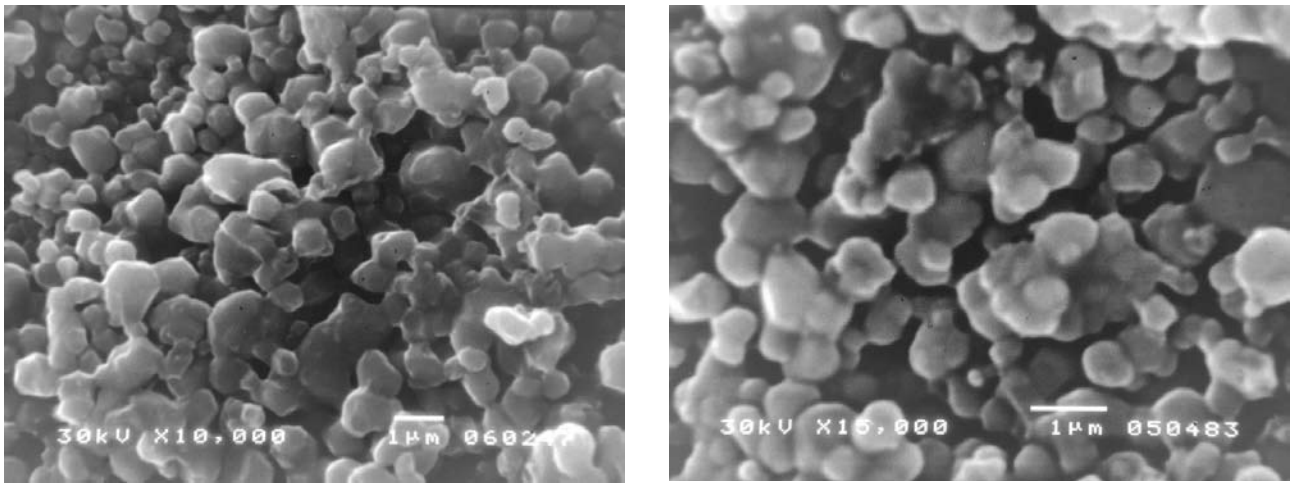

a) b)

Figure 1. SEM images of La-doped $BaTiO_3$ sintered at 1320°C: a) 0.1 La-BT and b) 1.0 La-BT

La/Mn doped $BaTiO_3$ in function of different amount of dopant concentration and sintering temperature. The modified Curie-Weiss law is used to clarify the influence of dopant on the dielectric properties and phase transformation in $BaTiO_3$.

II. Experimental

The samples of La/Mn-codoped $BaTiO_3$ ceramics were prepared by a conventional mixed oxide solid state reaction. Reagent grade $BaTiO_3$, (Ba/Ti = 0.996±0.004, Rhone Poulenc, average particle size of 0.10−5 μm), La_2O_3 and MnO_2 (Merck, Darmstadt), were used as starting materials. The content of La_2O_3 ranged from 0.10 to 5.0 at% and that of MnO_2 was kept constant at 0.05 at%. The specimens are denoted such as 0.10 La-BT for specimen with 0.10 at% La and 0.05 at% Mn. The starting powders were homogenized in ethanol medium with alumina balls for 24 h. After drying for several hours, the powders were pressed at 120 MPa into disks of 10 mm in diameter and 2 mm of thickness. The samples were sintered at 1320°C and 1350°C for two hours with heating rate of 300°C/h in air atmosphere. The bulk density was measured by Archimedes method. The microstructures of the sintered or chemically etched samples were observed by scanning electron microscope JEOL-JSM 5300 equipped with EDS (QX 2000S) system. Prior to electrical measurements silver paste was applied on flat surfaces of specimens. Capacitance was measured using HP 4276 LCZ meter and the variation of dielectric constant with temperature was measured in a temperature interval from 20 to 200°C.

III. Results and discussion

3.1 Microstructure characteristics

Densities of the La-doped samples varied from 70 to 80 % of theoretical density of $BaTiO_3$ (TD_{BaTiO3} = 6.02 g/cm^3), being lower for higher dopant additive for both sintering temperatures. The homogeneous and completely fine-grained microstructure with grain size ranged from 1.0−3.0 μm, without any indication of abnormal grains, is the main characteristics of low-

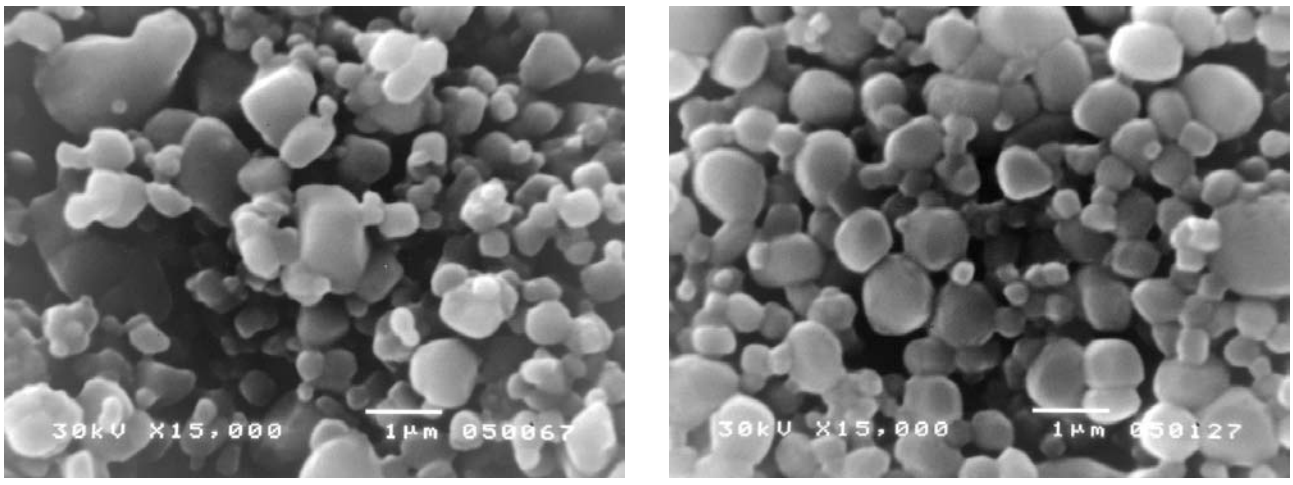

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Figure 2. SEM images of specimens sintered at 1350°C: a) 0.1 La-BT and b) 1.0 La-BT

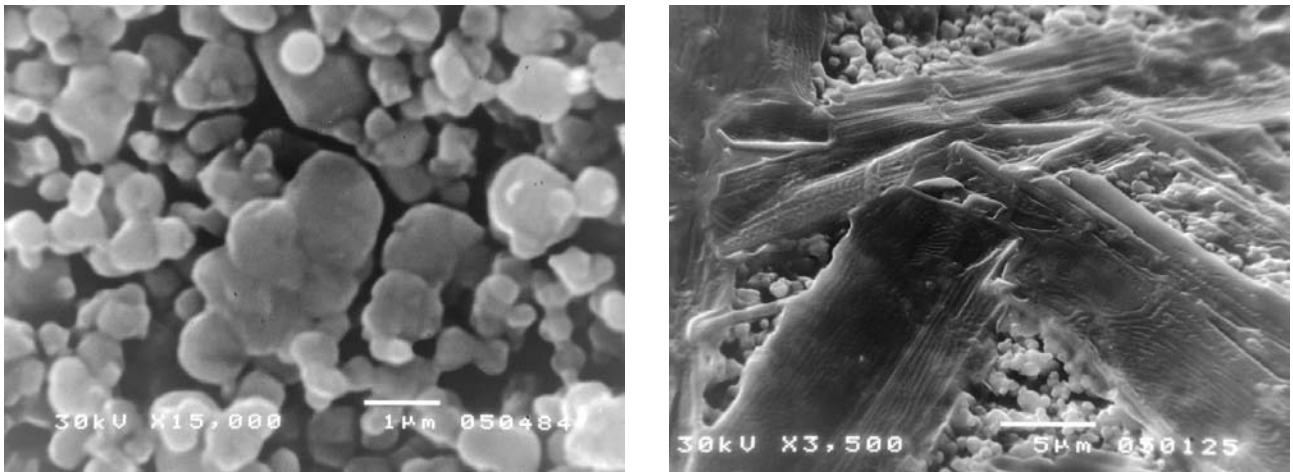

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Figure 3. SEM images of specimens sintered at 1350°C taken from the same specimen: a) fine grained matrix and b) secondary grain growth in fine grained matrix

er doped La-$BaTiO_3$, sintered at 1320°C (Fig. 1). The similar microstructure with grain size around 3.0 μm is observed in 0.1 and 0.5 at% La-$BaTiO_3$ specimens sintered at 1350°C (Fig. 2). With the increase of dopant amount the increase of porosity is evident.

However, the microstructure in highly doped La-$BaTiO_3$ samples sintered at 1350°C was quite different from that observed in lower doped samples. In 1.0 at% La-BT samples sintered at 1350°C, at temperature which is above eutectic point, apart from the fine grained matrix (Fig. 3a), some local area with long elongated grains and secondary abnormal grains with serrated boundaries (Fig. 3b) and domain structure were observed (Fig. 4).

Regarding the domain structure, two types of domain structures can be seen, i.e. the directional long domains that pass through the entire grain with 90° domain boundaries (Fig. 4a) and randomly oriented domains within some individual abnormal grains (Fig. 4b). According to the qualitative EDS analysis the difference in microstructural features is due mainly to the inhomogeneous distribution of La_2O_3. EDS spectra taken from different area in the same sample indicated that the La-rich regions are associated with small grained microstructure (Fig. 5a), whereas EDS spectra free of La-content, corresponded to the abnormal grains with domain structure (Fig. 5b). The XRD pattern (Fig. 6) shows a crystalline phase which is consistent with a perovskite-type structure. There is no evidence of any secondary phases. At 1350°C a liquid phase sintering, with inhomogeneous distributed liquid phase, contributes to the secondary abnormal grain growth. The poor additive dispersion also contributes to the non uniformity of domain alignment. The similar microstructures with secondary abnormal grains and domain structure were also found in samples doped with 2.0 or 5.0 at% La. The role of La_2O_3 as grain growth inhibitor prevails in heavily doped samples.

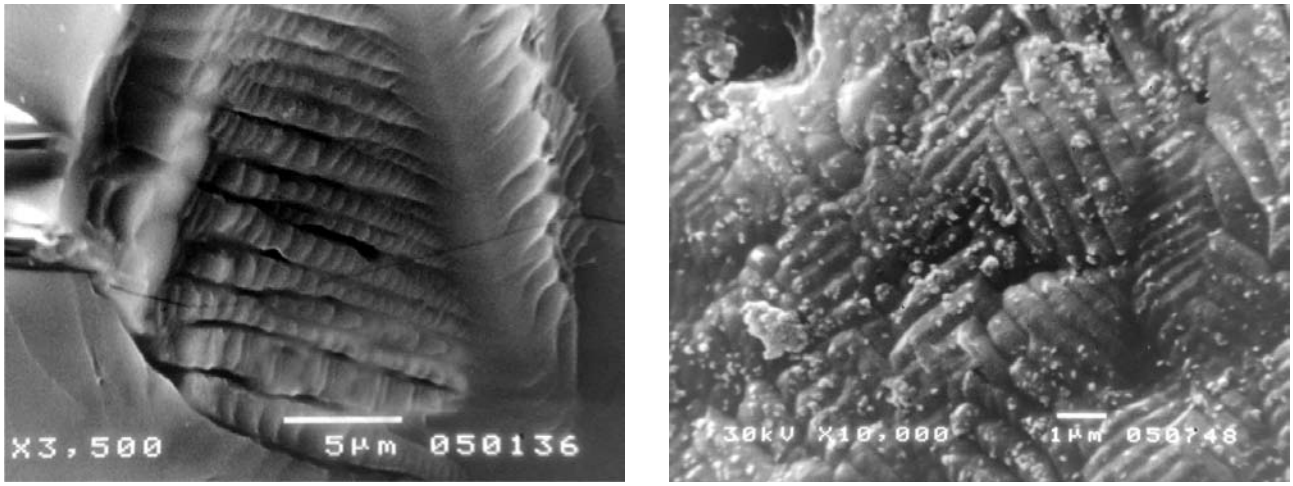

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Figure 4. SEM images of domain structure in 1.0La-BT sintered at 1350°C: a) serrated grain boundaries, b) randomly oriented domains

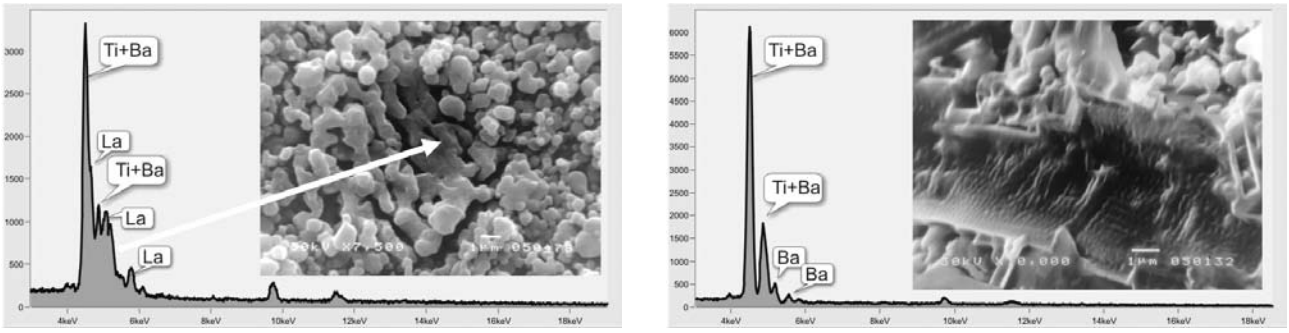

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Figure 5. EDS spectra of 1.0 at% La-$BaTiO_3$ sintered at 1350°C: a) local area reach in La associated with fine grained matrix and b) grains with domain structure free of La

3.2 Dielectric characteristics

Regarding the electrical resistivity, all samples sintered at 1320°C and 1350°C, are electrical insulators with a resistivity $\rho > 10^8$ Ωm at room temperature. It is believed that ionic compensation mechanism is exclusively involved and due to immobility of cation vacancies at room temperature the doped samples remain insulating. Also, in small grained microstructure, the thickness of grain boundary insulating layer becomes comparable to the size of grains and therefore the resistivity is very high [2,4]. In addition, the effective carrier density is reduced owing to the presence of Mn-acceptor.

The effects of additives on the dielectric behaviour of modified $BaTiO_3$ can be analyzed through permittivity-temperature dependence given in Fig. 7. The variation in dielectric permittivity behaviour hardly can be related only to the differences in microstructure, since the grain sizes are similar in most of the specimens. The observed variation in permittivity could be associated with the La accumulation at grain boundaries that causes a high resistivity of samples too. The dielectric constant for all investigated samples decrease with increase of La content and increase with increase of sintering temperature. Among the investigated La-doped samples, the highest value of dielectric permittivity of ε_r = 3300 at room temperature and ε_r = 5000 at Curie temperature and the greatest change with temperature were measured in 0.1La-BT sintered also at 1350°C.

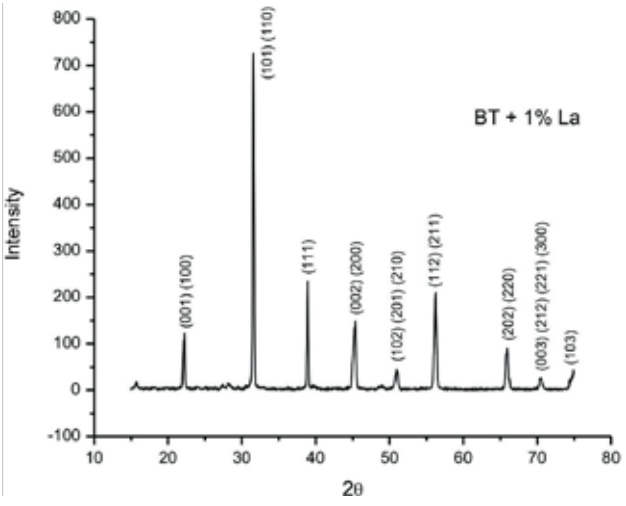

Figure 6. X-ray diffraction pattern for 1.0 at% La-BT shows a perovskite-type structure, there is no evidence of any secondary phase

The results in Fig. 7 show a small variation in dielectric permittivity at room and Curie temperature and nearly flat and stable permittivity response of dielectric constant for samples with higher lanthanum amount. The decrease in dielectric constant in La-doped samples with the increase of dopant concentration, are due firstly, to the decrease in density and secondly, to the nonhomogeneous distribution of additive throughout the specimens.

The shapes of the curves, presenting the decrease of dielectric constant with the increase of dopant concentration, (Fig. 8a and 8b) are similar to that ones presenting the theoretical density dependence of La-content (Fig. 8c).

From the permittivity-temperature measurements Curie temperature was in the range of 126–129°C being lower for lower doped La-$BaTiO_3$. The Curie-Weiss law was used to calculate the dielectric parameters such as Curie constant (C) and Curie-Weiss temperature (T_0). The Curie constant (C) decreases slightly with the increase of additive amount and have an extrapolated Curie-Weiss temperature (T_0) down to very low temperature [13]. In low doped samples, that exhibit a small grained microstructure and high density, the Curie constant is higher compared to the high doped samples.

In order to investigate the Curie Weiss behaviour the modified Curie-Weiss law is used [14]:

$$\frac{1}{\varepsilon_r} = \frac{1}{\varepsilon_m} + \frac{(T - T_m)^\gamma}{C'} \qquad (1)$$

where ε_r is dielectric constant, ε_m maximum value of dielectric constant, T_m temperature where the dielectric value has its maximum, γ critical exponent for diffuse phase transformation (DPT) and C' the Curie-Weiss-like constant. The parameters calculated according to the Curie-Weiss and modified Curie-Weiss law are given in Table 1.

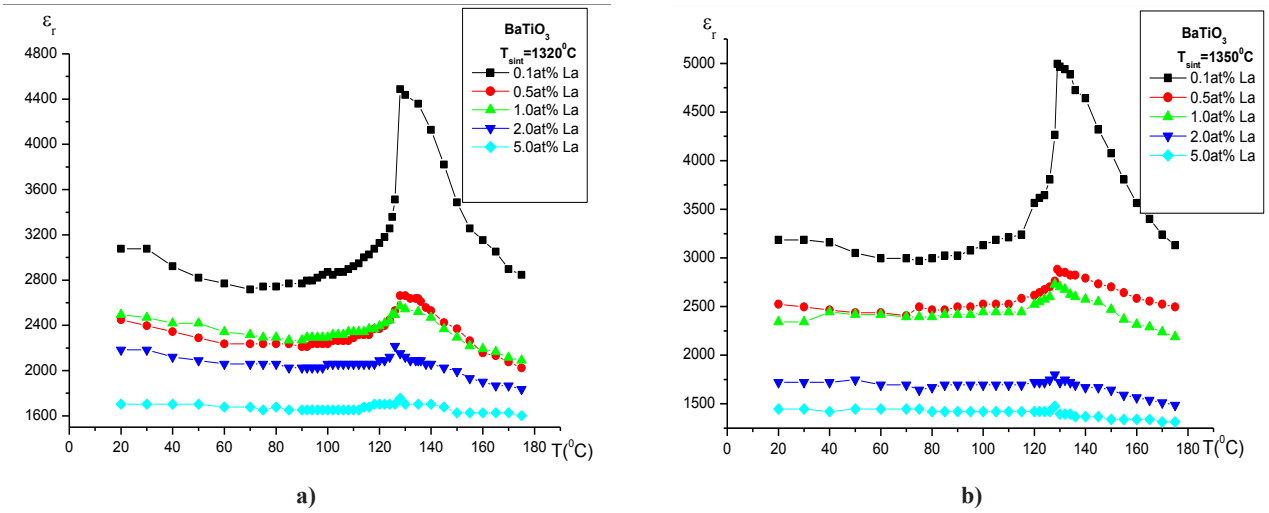

Figure 7. Dielectric constant of La-doped $BaTiO_3$ in function of temperature: a) samples sintered at 1320°C and b) samples sintered at 1350°C

The critical exponent γ is calculated from the best fit of the curves $ln(1/\varepsilon_r - 1/\varepsilon_m)$ *vs.* $ln\,(T-T_m)$ where γ represent the slope of the curve. According to [14] the critical exponent γ for $BaTiO_3$ single crystal is 1.08 and gradually increases up to 2 for diffuse phase transformation in modified $BaTiO_3$. For low concentration of dopant the critical exponent γ is in the range from 1.0 to 1.19. The low values of γ ($\gamma \approx 1$) could be predicted from the shape of ε_r vs. T plots which showed the sharp phase transition from ferroelectric to paraelectric phase

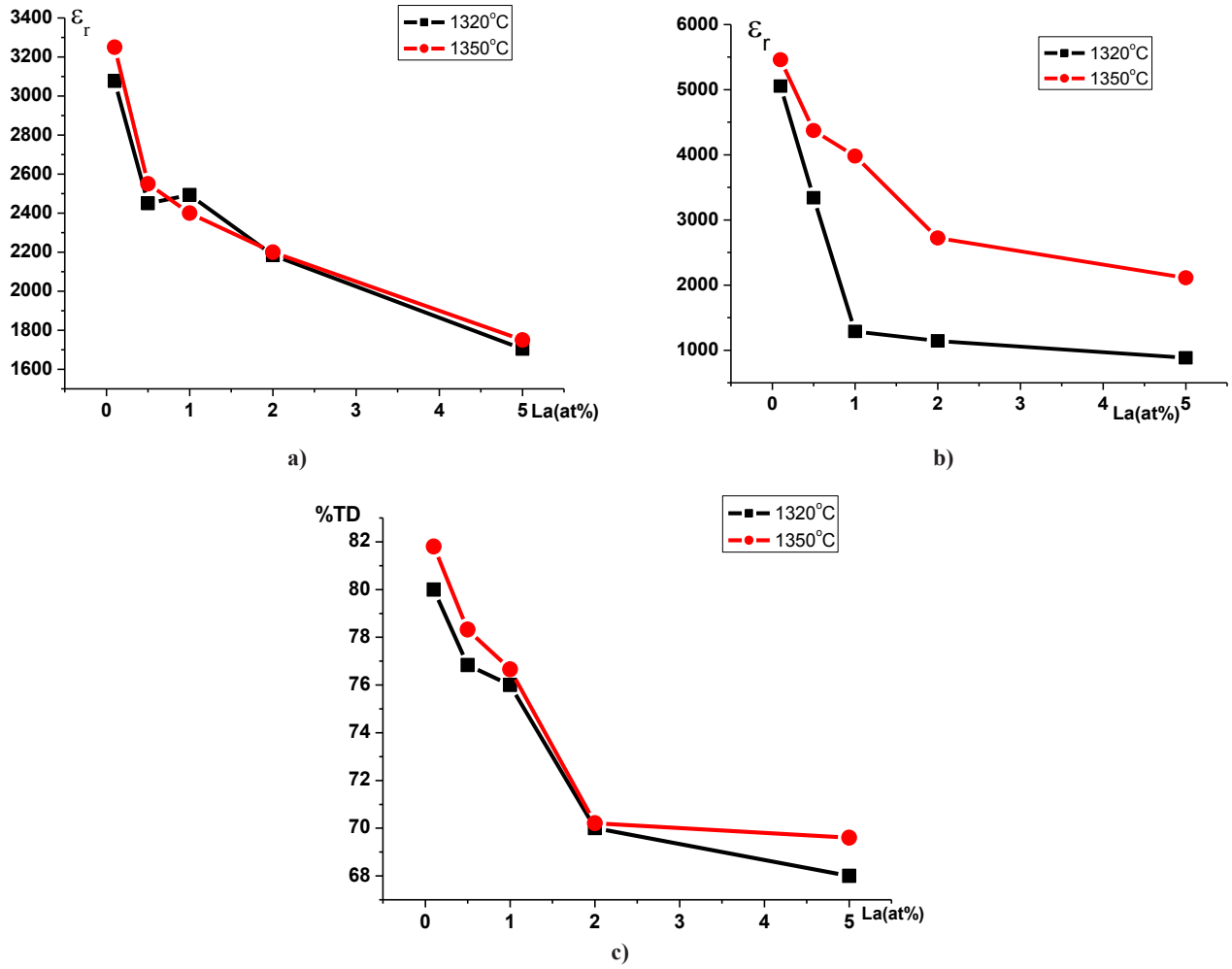

Figure 8. Dielectric constant in function of La-content: a) measured at room temperature, b) measured at Curie point and c) relative density in function of La-content

Table 1.The parameters calculated according to the Curie-Weiss and modified Curie-Weiss law

La-content [at%]	T_{sint}=1320°C			T_{sint}=1350°C		
	C [10^5K]	γ	C' [10^5K]	C [10^5K]	γ	C' [10^5K]
0.1%	9.91	1.01	1.53	8.39	1.01	1.39
0.5%	5.63	1.02	3.75	8.21	1.02	1.89
1.0%	4.90	1.19	8.71	5.19	1.12	4.23
2.0%	3.53	1.36	11.3	4.44	1.13	4.85
5.0%	3.31	1.50	16.3	3.65	1.40	5.01

at Curie point. The critical exponent γ slightly increases with the increase of additive concentration, pointing out a diffuse phase transformation for heavily doped samples. The highest value of γ (γ = 1.50) was calculated in 5.0 at% La doped samples sintered at 1320°C.

IV. Conclusions

The relative density in La/Mn doped ceramics ranges from 70–80 % of TD, and decreases with dopant content. In general, although there is a significant difference in porosity predominantly small grained microstructures with grains 1.0–3.0 μm in size were obtained. All samples, independent of sintering temperature, have a resistivity of 10^8 Ωm at room temperature. The differences in ε_r values in low and heavily doped La/Mn ceramics are due firstly, to the different porosity of doped ceramics and secondly, to the presence of La -rich regions and formation of secondary abnormal grains. The different domain patterns are revealed in abnormal grains. The highest dielectric constant at room temperature was measured in 0.1 at % La-$BaTiO_3$ (ε_r = 3300), being as high as 5000 at Curie temperature, for samples sintered at 1350°C. The transition mean temperature is in the range from 126°C to 129°C. The diffuse phase transformation characterized the heavily doped ceramics. A nearly flat and stable permittivity response was observed in specimens with 2 and 5 at% of dopant content.

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