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Influence of lanthanum and niobium doping on the relaxor behaviour of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics

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Abstract

The lead–barium–zirconate–titanate (PBZT) ceramics of composition (Ba/Zr/Ti: 25/70/30) exhibit classical relaxor ferroelectric behaviour similar to other complex lead perovskites such as lead–lanthanum–zirconate–titanate or lead–magnesium–niobiate. Influence of Nb or La admixture on grain structure, dielectric and pyroelectric properties was showed earlier. The effect of simultaneously lanthanum and niobium modified PBZT 25/70/30 ceramics on properties have been studied and compared with earlier results. The influence of the additives on the values of characteristic parameters describing the relaxor behaviour of the studied ceramics (ε'_{max}, T_m, T_f, T_B) was determined.
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1. Introduction

The investigation of (Pb,Ba)(Zr,Ti)O_3 system (PBZT) were initiated by Smolenskii et al. [1]. The structural and dielectric measurements, carried out by Ikeda [2], show that the structural phase transitions, occurring in these ceramics, and their dielectric properties are strongly dependent on both the Zr/Ti ratio and Ba contents. The measurements of dielectric characteristics and electric field induced strain properties, recently carried out by Li and Heartling [3], confirmed the phase diagram proposed by T. Ikeda. Moreover, these measurements showed that for certain compositions, the behaviour of these ceramics is typical for the relaxor ferroelectrics. Our investigations focus on the PBZT ceramics with Zr/Ti ratio equal 70/30 and Ba contents 25. The results were presented earlier in [4]. We also investigated the influence of heterovalent additives on relaxor properties of the mentioned ceramics. The problems of La-modified and Nb-modified were widely considered in our previous papers [5,6]. It was assumed, that the substitution of La^{5+} ions for Pb^{2+} or Ba^{2+} ion in the A-site of the perovskite structure [7] is the most likely phenomena, while the Nb^{5+} ions occupied the place of Zr^{4+} or Ti^{4+} in B-site of mentioned crystal lattice [8–11]. Electrical neutrality is maintained by forming A-site or B-site vacancies, respectively. Both additives significantly changed the grain structure, dielectric and pyroelectric characteristics of PBZT ceramics. Their strong influence on the properties characteristic for ferroelectric relaxors was also written down. Those results encouraged us to prepare the ceramics with both admixtures simultaneously. We expected much more significant changes as well as the improvement of the relaxors' properties of our interest. The results obtained for the new ceramics, and their comparison with the earlier investigated ones, are reported in the present paper.

2. Sample preparation

The PBZT ceramics of composition 25/70/30 pure and doped by La an Nb were prepared by using the conventional mixed-oxide sintering technique. The proper amounts of reagents: PbO, $BaCO_3$, TiO_2, ZrO_2, La_2O_5 and Nb_2O_5 were weighed and mixed. Three kinds of composition were studied: ceramics doped by 0–4 at.% La (PBZT La), ceramics doped by 0–4 at.% Nb (PBZT Nb) and ceramics doped 0–1 at.% La and Nb (PBZT La,Nb). Details of sample preparation were the same as reported previously [5,6]. Table 1 summarizes the sintering conditions. The table shows that the admixture of niobium requires extension of time of third sinter and increase the temperature of the sinter. The third sintering was necessary,

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Table 1
Sintering conditions

	Samples							
	PBZT *x*/70/30		PBZT 25/70/30 + *x* at.% La		PBZT 25/70/30 + *x* at.% Nb		PBZT 25/70/30 + *x* at.% La and Nb	
	Temperature (°C)	Time (h)	Temperature (°C)	Time (h)	Temperature (°C)	Time (h)	Temperature (°C)	Time (h)
Sintering								
I sintering	925	2	925	2	925	2	925	2
II sintering	1250	4	1250	4	1250	4	1250	4
III sintering	1300	7	1300	10	1360	10	1360	10

because considerably improved the quality of investigated ceramics, which became harder. Additionally, after third sintering, the density of investigated ceramics increased insignificantly (for example: the density of PBZT 25/70/30 ceramics co-doped by 1 at.% La and Nb changed from 6.3 to 6.9 g/cm^3 for ceramics after second and third sintering, respectively.

The Archimedes displacement method with distilled water was employed to evaluate sample density. The results are given on Fig. 1. This figure shows that the addition of lanthanium and niobium oxide improved the quality of ceramics. Additionally, this thesis confirmed the structure researched by using the scanning electron microscope JSM-5410 with an energy dispersive X-ray spectrometer (EDS). The grain size measurements were performed on structure surface of the ceramics. The grain size of pure ceramics was ca 15 μm. Porosity of those ceramics was about 5% [4]. Addition of lanthanium dopand caused decrease of grain size from 10 μm to less 5 μm for 1 and 4 at.% La, respectively. Porosity of La-modified ceramics was much smaller (less 5% for 4 at.% La) than the undoped samples. In the case of ceramics doped by Nb the average grain size could not be precisely determined, because when the content Nb was equal 1 at.% in ceramics appeared two kinds of grains, significantly different with size. Similar behaviour was observed in case of $PbZrO_3$ and PZT ceramics [12]. Porosity of Nb-modified ceramics is insignificantly smaller than undpoped ceramics (7% for PBZT 25/70/30 ceramics doped by 4 at.% of Nb). In case of PBZT 25/70/30 ceramics co-doped by La and Nb two kinds of grains, mentioned above, appeared when the concentration of both additives was also equal 1 at.% (Fig. 2), but the number of the smallest grains was lower in comparison with the ceramics PBZT doped 1 at.% of Nb. The porosity of co-doped by La and Nb ceramics was comparable with ceramics modified by Nb.

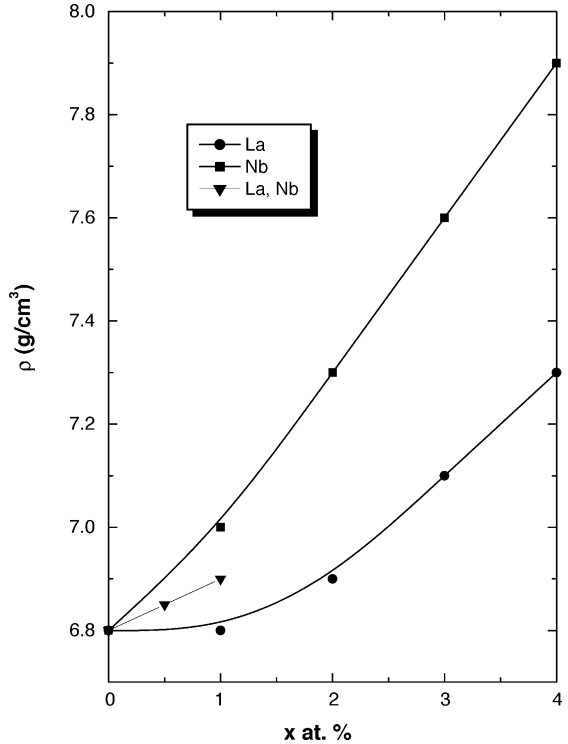

Fig. 1. The sample density of PBZT 25/70/30 ceramics with various La or Nb, as also La and Nb contents.

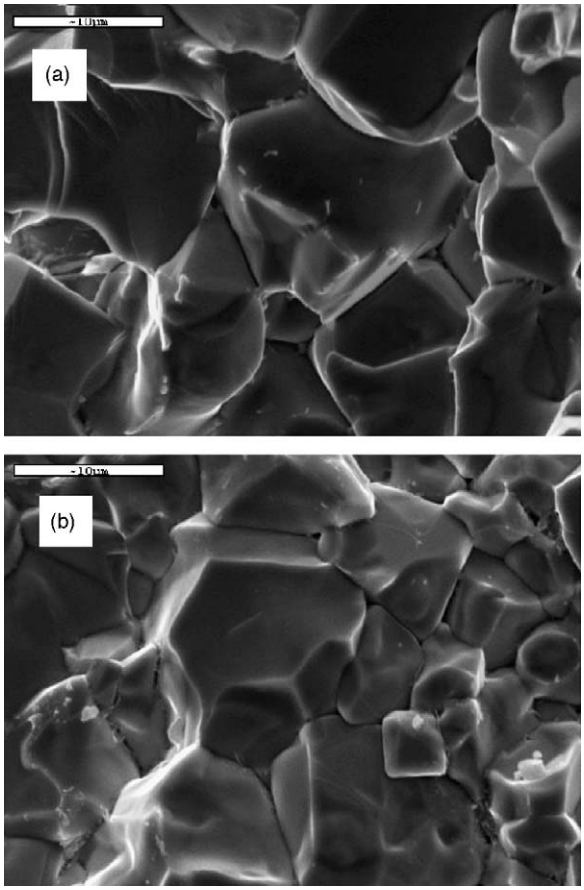

Fig. 2. Scanning electron microscope images of the fracture surface of PBZT 25/70/30 ceramics with La and Nb contents 0.5 at.% (a) and 1 at.% (b).

The samples of appropriate size were prepared for dielectric measurements. The cut and polished samples were coated with silver electrodes, using a silver paste, without thermal treatment.

3. Experimental

Samples 0.6 mm thick were used for measurements of dielectric constant as a function of temperature. The automatic measuring system with HP 4192A impedance analyser was used to measure and record ε' and tan δ numerically. They were performed in successive heating–cooling cycles with a constant rate of 2 K min^{-1}. The samples were deaged by thermally treatment at 700 K for 2 h prior to measurements. Part of the frozen defects, formed during the sintering process, recombined and the tensions caused by mechanical treatment relaxed.

The comparison of characteristic $\varepsilon'(T)$ and tan $\delta(T)$ curves, measured at 1 kHz frequency, for all studied ceramics undoped, doped by 1 at.% of La or Nb and also co-doped by 0.5 and 1 at.% La and Nb (as example) is shown in Fig. 3a and b, respectively. All investigated ceramics show great value of ε', although its increase is the highest when the content of admixture is equal 1 at.%. The temperature T_m corresponds to the maximum of dielectric constant in all case shifts to the lowest value.

The pure PBZT 25/70/30 ceramics exhibit properties typical for ferroelectric relaxors. Namely all the $\varepsilon'(T)$ curves measured at various frequencies show the reduction of ε'_{max} and shift of the corresponding temperature T_m with the frequency increase. Similar behaviour was observed in case of doped ceramics. We made an attempt of describing the degree of frequency dispersion through the value of $\Delta\varepsilon'_{max}$ (was defined here as the difference between the ε'_{max} measured at 0.1 kHz and that measured at 20 kHz) and ΔT_m (defined in the similar manner). The value of $\Delta\varepsilon'_{max}$ and ΔT_m increased with admixture concentration (Fig. 4). However, for ceramics doped by Nb and La simultaneously this increase was far greater. The tan $\delta(T)$ curves behaviour (Fig. 3b) is characteristic for relaxor ferroelectric, the minima in their course, corresponding to the temperature of FE-PE phase transition in ''normal'' ferroelectrics, are shifted upwards in relation to the temperatures T_m (see Fig. 3a)

The observed frequency dependence of T_m was empirically evaluated by using the Vogel–Fulcher relationship, adopted from the theory of magnetic relaxation in spin glass systems:

$$\omega = \omega_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right] \quad (1)$$

where E_a is the activation energy, T_f is the freezing temperature of polarisation fluctuation, and ω_o is the pre-exponential factor. The values of E_a increased with niobium or lanthanum content, in case of ceramics simultaneously modified by both additives the value decreased (see Fig. 5b). The temperature T_f decreasing (see Fig. 5a) in all cases, but the decrease of T_f in case of La and Nb modified ceramics was more significant. We also made an attempt of determining the Burn's temperature (T_B) with the help of the equation proposed by Kirkpatric and Sherrington [13]

$$\varepsilon'(T) = \frac{C\{1 - q(T)\}}{T - \theta\{1 - q(T)\}} \quad (2)$$

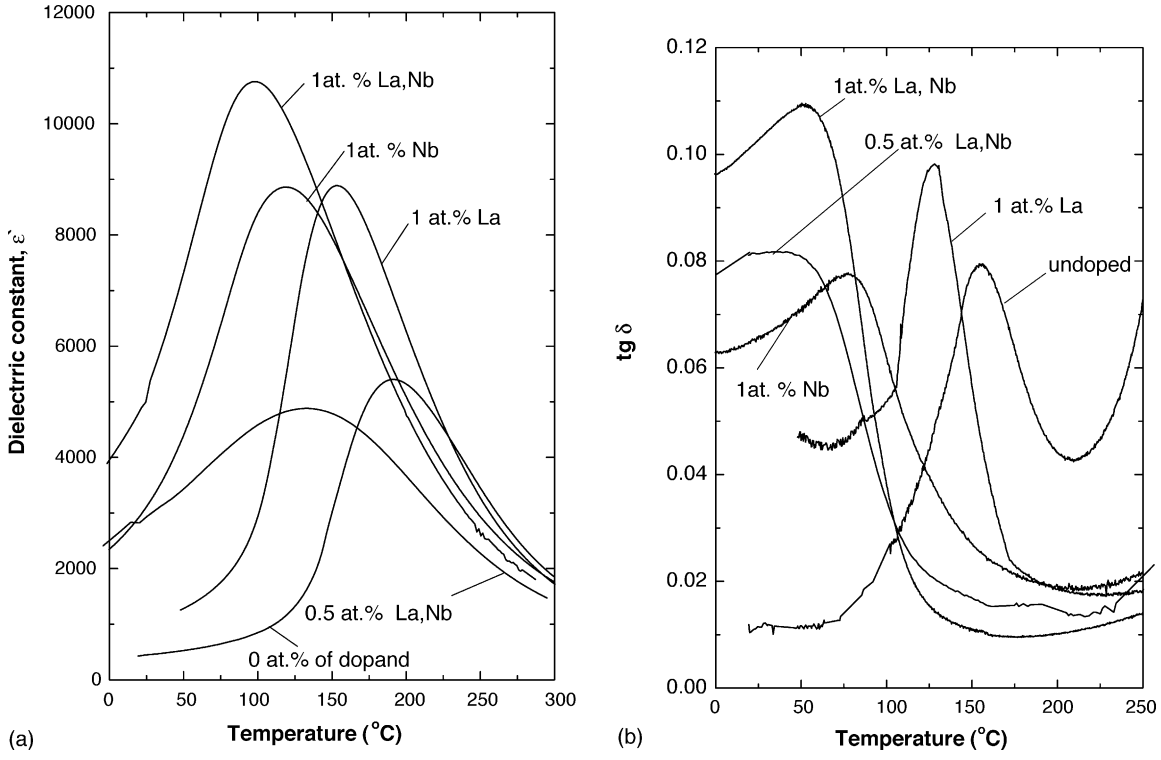

Fig. 3. Dielectric constant (a) and loss factor tan δ (b) as a function of temperature, measured at frequency 1 kHz, for PBZT 25/70/30 ceramics with various 1 at.% La, 1 at.% Nb, as also 0.5 and 1 at.% La and Nb contents.

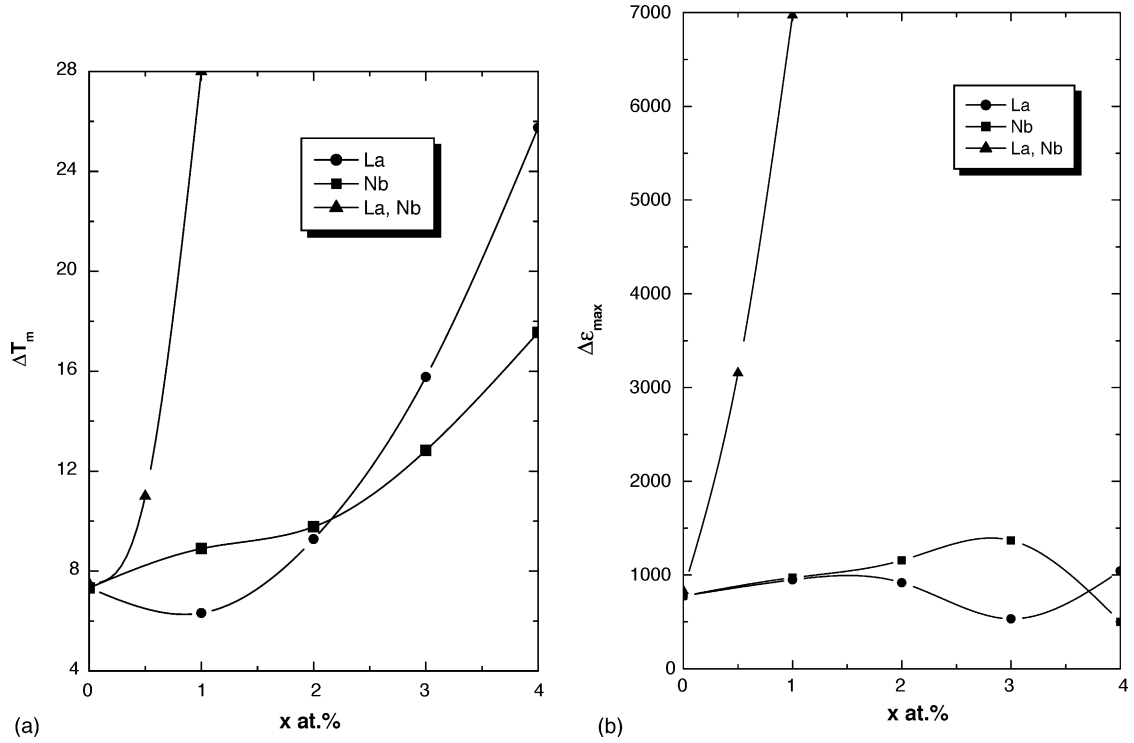

Fig. 4. Degree of frequency dispersion of (a) $\Delta T_m = T_m$ (20 kHz) $- T_m$ (0.1 kHz) and (b) $\Delta\varepsilon'_{max} = \varepsilon'_{max}$ (0.1 kHz) $- \varepsilon'_{max}$ (20 kHz) as a function of admixture concentration.

The equation is a modified Curie–Weiss formula, where θ is the Curie–Weiss temperature, C is the Curie–Weiss constant and $q(T)$ is the temperature dependent local order parameter, which is equal to zero at the temperature where the polar clusters begin to appear on cooling (T_B). In case of PBZT 25/70/30 ceramics doped by lanthanum temperature T_B increased from 302 to 375 °C for ceramics with 1 and 4 at.% of La, respectively, while for Nb doped T_B did not reveal any systematic changes. For the ceramics with $x \leq 2$ the temperature T_B increased, but for larger concentration of niobium the T_B decreased to the value of $T_B = 330$ °C for $x = 4$. The lanthanum and niobium added to pure ceramics simultaneously caused significant decrease of the temperature T_B (from 300 °C for pure ceramics to 258 °C and 231 °C for $x = 0.5$ at.% La,Nb and $x = 1$ at.% La,Nb, respec-

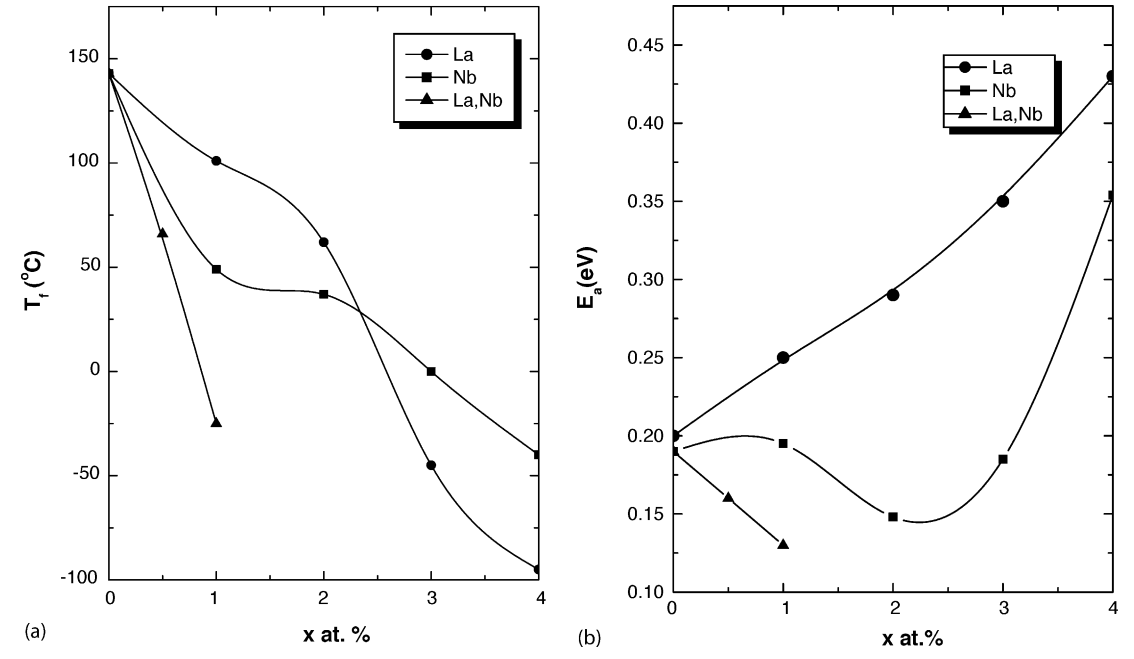

Fig. 5. (a) The freezing temperature (T_f) and (b) activation energy (E_a) as a function of admixture content in PBZT 25/70/30 ceramics.

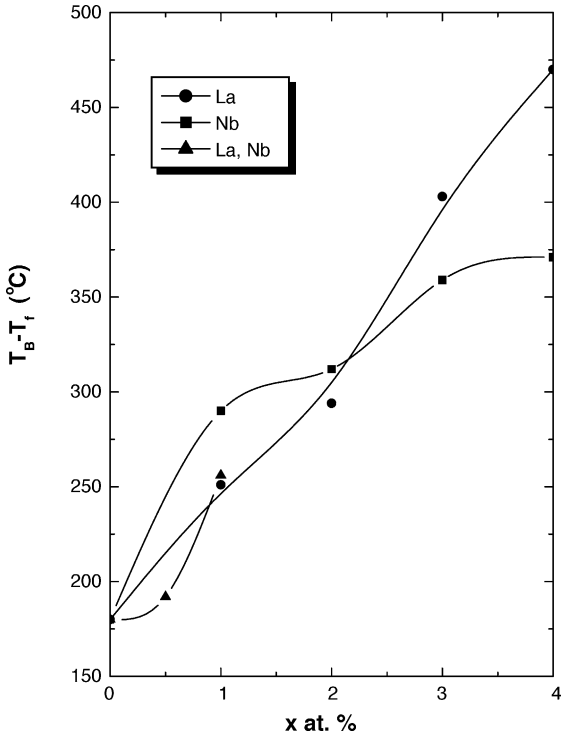

Fig. 6. The difference between the Burn's (T_B) temperature and freezing temperature (T_f) as a function of admixture content in PBZT 25/70/30 ceramics.

tively). Mentioned above changes of the temperatures T_f and T_B in consequence caused widening of the temperatures range of appearing the characteristic properties of ferroelctric relaxor (Fig. 6), but not so significantly as in case of ceramics madyfied by La and Nb separately.

4. Discussion

The experimental data obtained for PBZT ceramics doped by La or Nb ions presented in our prior papers showed, that addition of cations in A or B sublattice caused not only a shift in temperature T_m, but also a considerable improvement of relaxor properties [5,6]. We assumed, that ions La^{3+} substitute for Pb^{2+} or Ba^{2+}. We supposed also that in case of Nb additive the substitution of Nb^{5+} ions for Zr^{4+}/Ti^{4+} ions is the most likely phenomena. In both cases, the electrical neutrality is maintained by forming A-site or B-site vacancies. Introduction of admixture on both sublattices leads to expansion of the chemical disorder connected with increased amount of vacancies. It seems very probable, that this fact is responsible for improvement of the relaxor behaviour in all investigated PBZT ceramics. It is commonly known that the dielectric behaviour of Pb containing relaxor ferroelectrics is generally explained in the literature in terms of small regions of local spontaneous polarisation (so called polar-regions) with a nanometer scale size [14]. The regions appear on cooling at the temperature T_B, much higher than T_m and their density increases with decreasing temperature. The decreasing temperature causes the increase of both: the number of polar-regions, as well as their size. Distribution of the relaxation times depends on the distribution of the size and polarisation strength of the polar-regions. The La and Nb-dopant probably reduces not only the grain size but also the size of polar-regions. It is very possible, that the size of nano-regions is diverse. It leads to the broadening of relaxation time and increases the degree of frequency dispersion (Fig. 4).

Origin of the mentioned regions is caused by the structural disorder. In lead containing relaxor ferroelectrics of the perovskite structure (ABO_3) two kinds of the structural disorder are taken into consideration: chemical disorder of A- and B-site and also A-site dynamical disorder, caused by the anharmonic motion of the Pb atoms [15]. The Nb^{5+} addition to PBZT ceramics changed both types of disorder. The same problem appears when the ions of lanthanum are added to ceramics.

5. Conclusion

In conclusion the dielectric behaviour of co-doped Niobium and lanthanum PBZT 25/70/30 ceramics have been measures and compared with the same behaviour of PBZT 25/70/30 ceramics pure and doped onlu by Nb or La. All investigated ceramics show behaviour typical for ferroelectric relaxors. All $\varepsilon(T)$ curves measured at various frequencies show the reduction of ε_{max} and shift of the corresponding temperature T_m to higher values with frequency increase. The behaviour is more distinct for doped ceramics, especially for ceramics co-doped by La and Nb. The value Burn's temperature and freezing temperature changed in the way that the temperature range of appearance of relaxors behaviour is broadened. The observed change in properties of pure and doped ceramics could be connected with increased of concentration Pb-vacancies.

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