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INVESTIGATION OF La^{3+} DOPING EFFECT ON PIEZOELECTRIC COEFFICIENTS OF BLT CERAMICS

Effects of La^{3+} admixture in barium lanthanum titanate (BLT) ceramics system with colossal permittivity on performance of prospective piezoelectric cold plasma application were studied. Usage of cold atmospheric pressure plasma appears promising in terms of industrial and healthcare applications. Performed investigation provide consistent evaluation of doping lanthanum amount on piezoelectric coefficients values with simultaneous capability of charge accumulation for effective plasma generation. Modification of ferroelectric materials with heterovalent ions, however with the lower radii than the original atoms, significantly affects their domain mobility and consequently electromechanical properties. To determine the piezoelectric coefficients, the resonance-antiresonance method was implemented, and values of piezoelectric and dielectric parameters were recorded. Finally the results indicated that addition of 0.4 mol.% of La^{3+} ions to the ceramic structure maximally increased the values of piezoelectric coefficient to d_{33} = 20 pC/N and to huge dielectric constant to $\varepsilon_{33}{}^{T}$ = 29277.

Keywords: BLT, piezoelectric coefficients, lead-free piezoelectric ceramics

1. Introduction

Plasma sources are already being implemented in numerous applications in many branches of industry, where a cold (non-thermal) atmospheric pressure plasma is required. The most popular are healthcare applications e.g. surface cleaning, disinfection and odor reduction [1]. Plasma generators require high-voltage transformers or generators in the GHz range. Until now, in all existing solutions, the high-voltage power suppliers for plasma generation are typically designed in separate bulky casings for safety reasons. Fortunately the innovative battery-driven piezoelectric solutions are compact, lightweight and easy to handle [2].

Considering an efficient material for piezoelectric plasma generators lead zirconate titanate $Pb(Zr_{1-x}Ti_{x})O_3$ (PZT) perovskite material still has its leading position, due to its highest piezoelectric and electromechanical coefficients values. The practical implementation of lead-free materials, for such generators and other power devices, requires efficient doping strategy as well as domain or texture engineering. The precise La^{3+} doping amount for barium titanate (BT) ceramics is proposed to gain higher piezoelectric coefficients with preservation of huge colossal dielectric permittivity. La^{3+} ions, which have ionic radii of 1.17 Å, can be used to substitute for Ba^{2+} (with an ionic radius of 1.49 Å) [3,4]. The influence of La^{3+} doping on BT properties especially draw our attention, due to its high impact on the value of dielectric constant, which makes these ceramics prospective for many applications, that can take advantage of its parallel huge capacitance [5,6]. Our investigation focused on BLT ceramics, doped with various molar content of lanthanum namely: $Ba_{1-x}La_{x}Ti_{1-x/4}O_3$, (BLT ceramics). The molar percentages of dopant were x = 0.1, 0.2, 0.3, 0.4 and 0.5 in reference to composition mentioned above abbreviated to BLT0, BLT1, BLT2, BLT3, BLT4 and BLT5, respectively.

The first question to be raised in this paper relates to the possibility of obtaining desirable piezoelectric performance sufficient for the creation of efficient piezoelectric plasma generators with additional advantage of high capacitance. The second enquiry, which is partly a consequence of the previous one, should deliberate about how La^{3+} addition influences the most important energy conversion parameter – d_{33} piezoelectric coefficient.

2. Experimental

Barium titanate ceramics, pure and doped with La_2O_3, were prepared by conventional mixed oxide method. The polycrystalline ceramic samples of $Ba_{1-x}La_{x}Ti_{1-x/4}O_3$ (where x = 0, 0.001, 0.002, 0.003, 0.004 and 0.005) were synthesized using oxides TiO_2, La_2O_3 and a carbonate $BaCO_3$ (all Aldrich with 99.9% purity). Reagents were weighed respectively in stoichiometric

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ratio, placed in a milling jar, and then milled in planetary mill for $t = 24$ h in ethyl alcohol C_2H_5OH. After the paste was dried, the obtained powders were pressed into disk-shaped pellets with a diameter of d = 10 mm, and thickness of h = 1 mm at p = 30 MPa pressure. Then, the pellets were synthesized in an alumina crucible at T_S = 950°C for t_S = 2 h in air atmosphere. After the synthesis the process of milling was repeated, and the samples, of both pure and La-doped $BaTiO_3$ ceramics, were sintered in air, at T_1 = 1250°C, T_2 = 1300°C and T_3 = 1350°C, for t = 2 h, with heating and cooling rates of 5°C/min.

X-ray diffraction measurements at room temperature were performed to investigate the purity of the perovskite phases. They were executed with a diffractometer XRD Philips PW 3710 using a cobalt source ($CoK_{\alpha 1}$), providing X-rays with a wavelength of 1.789007 Å, with a scan step increment of 0.01° and with a counting time of 8 s/step, for $\Delta\ 2\theta$ ranged between 10° and 90° [7]. To estimate the structural characteristics (unit cell parameters, tetragonality factor and unit cell volume), the second scan was performed with step size 2θ = 0.02, and with a counting time of 4 s/step, for $\Delta\ 2\theta$ ranged between 10° and 120°. Parameters defining the position, magnitude and shape of the individual peaks were obtained using the pattern fitting and profile analysis using the PowderCell 2.4 program [8]. In order to measure the piezoelectric and ferroelectric properties, silver paste (P122) was placed on the polished samples as the electrodes and fired at T = 850°C for t = 15 min.

3. XRD characterization of the BLT samples

Fig. 1 shows the XRD patterns of the BLT ceramics, with the variation of lanthanum content in comparison to the pattern calculated from PDF database. They exhibit very good compatibility, as Goodness Of Fit parameter (GOF) is not exceeding 7. All BLT samples exhibited a tetragonal perovskite phase (P4 mm space group, No. 99) with traces of secondary phase (Fig. 1a,b) for BLT0 and BLT1, but the weight fraction not exceeding 0.75% (Fig. 1a,b). The lattice parameters for all samples were calculated using the Rietveld method, results are listed in Table 1. It is observed that the c/a ratio (tetragonality factor) is decreasing for

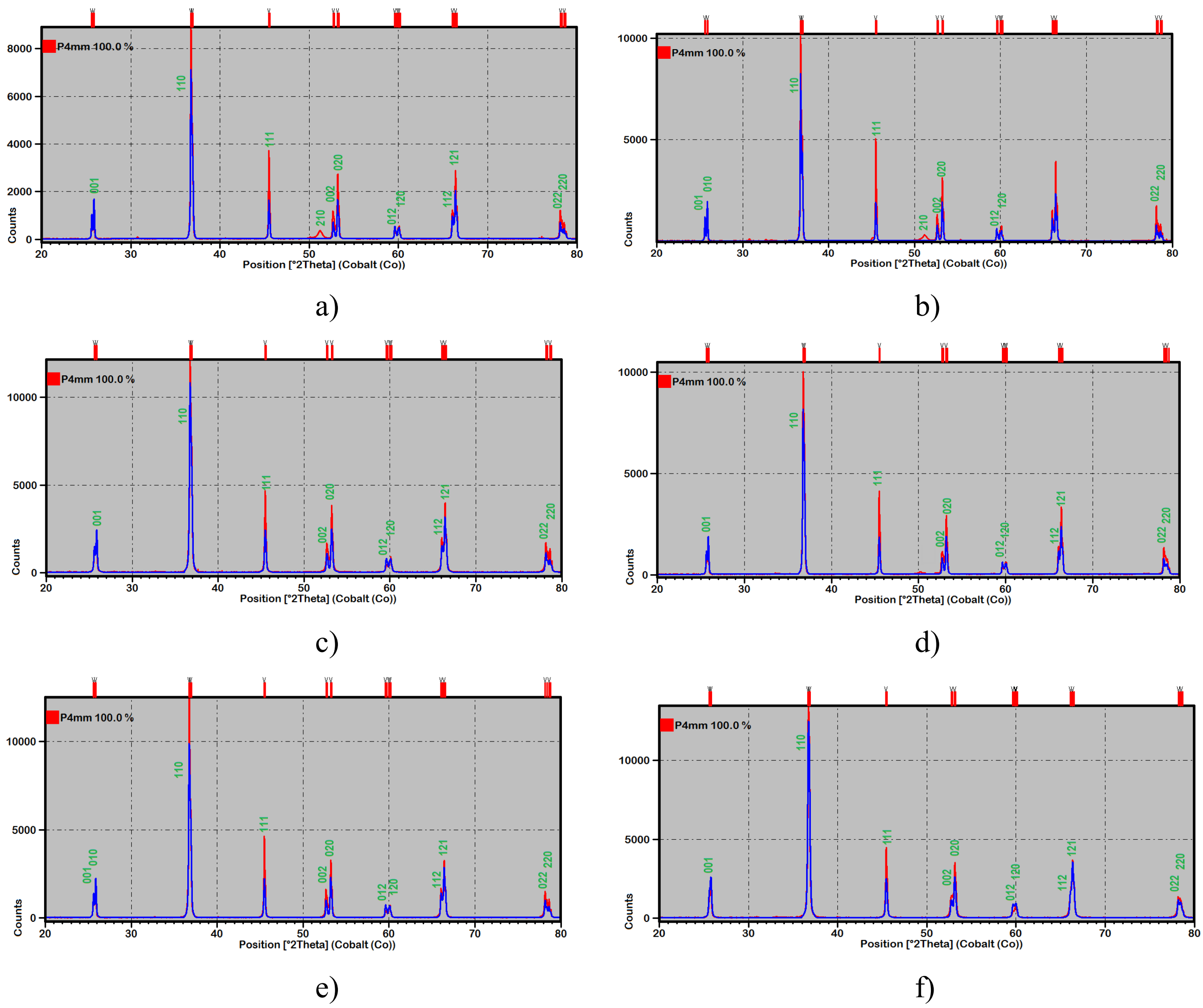


Fig. 1. XRD pattern of the BLT ceramics with the variation of lanthanum content in comparison to the calculated pattern from the PDF database. The spectra are presented respectively for BLT0 (a), BLT1 (b), BLT2 (c), BLT3 (d), BLT4 (e) and BLT5 (f)

TABLE 1

The sintering related coefficients for obtained BLT samples

Parameter	BLT0	BLT1	BLT2	BLT3	BLT4	BLT5
Density calculated (XRD) [g/cm^3]	6.0226	6.0204	6.0276	6.0279	6.0286	6.0371
Tetragonality (*c*/*a*)	1.0090	1.0103	1.0095	1.0083	1.0070	1.0068
a [Å]	3.9941(9)	3.9929(8)	3.9929(1)	3.9941(1)	3.9921(9)	3.9930(7)
c [Å]	4.0301(9)	4.0342(8)	4.0307(1)	4.0274(1)	4.0202(9)	4.0203(7)
Unit cell volume *V* [Å^3]	64.3599(6)	64.3158(7)	64.2347(1)	64.2347(7)	64.2044(5)	64.1419(9)
Peak shape parameter	0.68	0.72	0.68	0.70	0.76	0.60
Space group	P4 mm	P4 mm	P4 mm	P4 mm	P4 mm	P4 mm
GOF	6	5	5	7	4	3

raising La^{3+} content, indicating stronger coupling between Ba/La and Ti, which is likely to increase piezoelectric coefficients (Table 1). Theoretical density has the highest value for BLT5, what is associated with the lowest value of unit cell volume and the peak shape parameter that shows that the sample is the least defected (Table 1). Detailed analysis of the obtained ceramics crystal structure was presented by the authors in previous scientific publications on the synthesis, microstructure, crystal structure and dielectric properties of ceramics discussed [7,8].

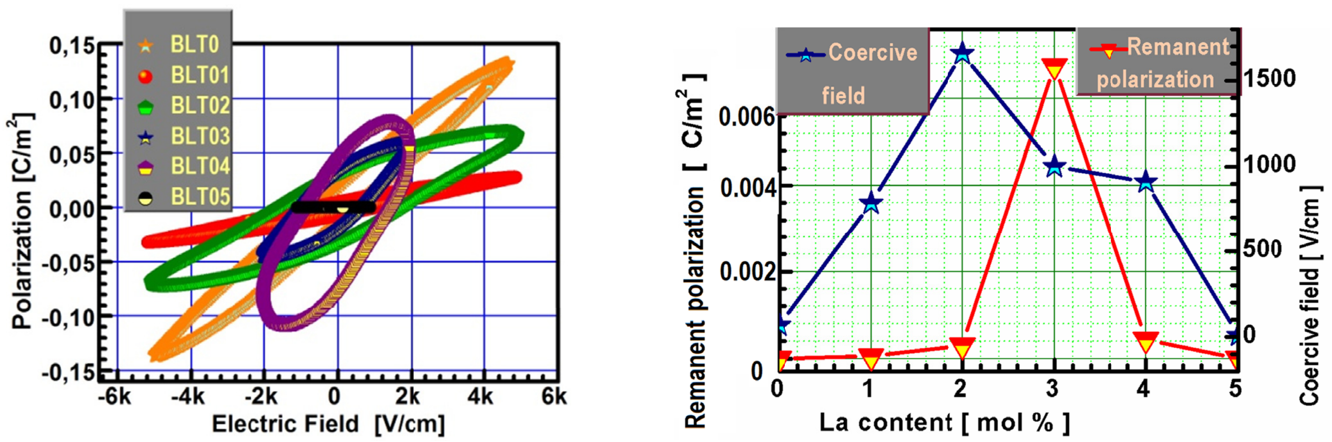
4. Ferroelectric properties

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as an indicator of the obtained BLT material properties. The "IEEE 180-1986 Standard Definitions of Primary Ferroelectric Terms" defines several reference points on the curve which enable numeric comparisons of materials. In many applications, especially with high frequency of applied field, there is strong requirement to switch polarization of ferroelectric materials with minimal coercive field and maximal remanent polarization. However, such a response is strongly dependent on crystal symmetries and grain orientations, but in a large extent also on polar defects structure, that is quite difficult to measure.

The polarization versus electric field (*P-E*) hysteresis loops with different La^{3+} content are shown in Fig. 2a. As it is visible in ferroelectric hysteresis loops the increasing amount of dopant dramatically change the shape of the loops from slim at low content, through thick at the admixture of 0.2-0.3 mol.% and finally to completely non ferroelectric shape at the 0.4 and 0.5 mol.% of dopant. Considering the characteristic parameters of ferroelectric hysteresis, namely the coercive field (E_c) and remanent polarization P_r the variation of lanthanum ratio in BLT ceramics causes creation of two maxima: it makes peak of P_r at 0.3 mol.% and E_c at 0.2 mol.% (Fig. 2b).

5. Piezoelectric parameters-characterization and discussion

The specimens were poled in a silicone oil bath under electric field of 30 kV/cm at poling temperature of 70°C for 15 min. After pooling an impedance frequency spectrum was measured using Agilent 4294A impedance analyzer (Fig. 3a) in the frequency range from 100 kHz to 1 MHz. The recorded extreme values of impedance modulus and phase allowed to determine piezoelectric coefficient variation by using the resonance/antiresonance method [9]. Additionally "quasi-static" ("Berlincourt") technique (ZJ-3C d_{33}-meter) was implemented



a) b)

Fig. 2. Hysteresis loop measured at a room temperature for BLT ceramics with different La^{3+} content (a); remanent polarization and coercive field dependency of La^{3+} admixture (b)

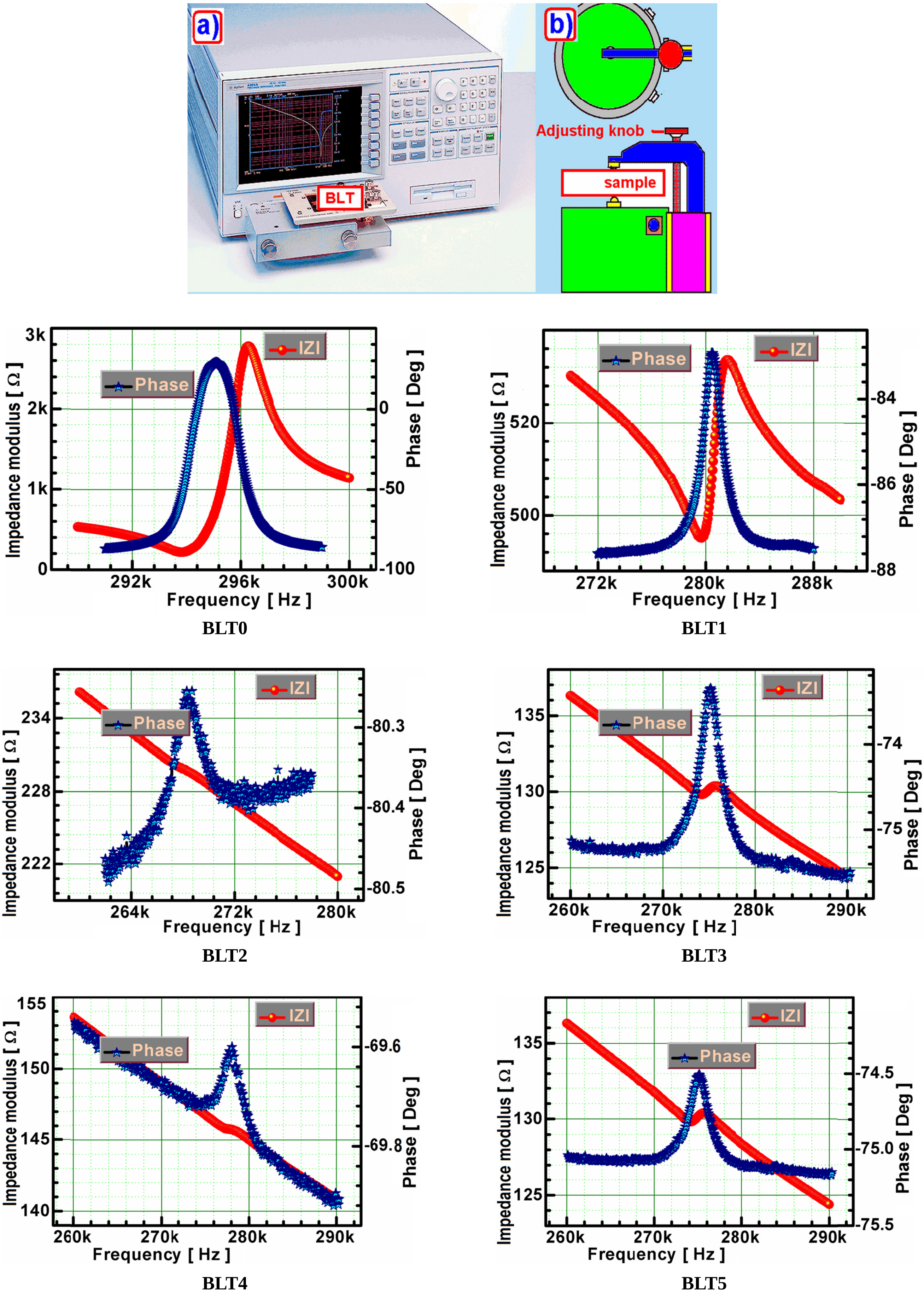


Fig. 3. The measurement setup with Agilent 4294A impedance analyzer (a) and ZJ-3C d_{33}-meter (b) and the recorded characteristics of impedance modulus and phase for fundamental resonance frequency range for BLT0, BLT1, BLT2, BLT3, BLT4 and BLT5

for direct d_{33} evaluation due to the fact that not all off higher resonances were detected by Agilent 4294A impedance analyzer especially for compositions with high permittivity values. The second method takes advantage from clamping the sample, subjecting it to a low frequency force, and final comparison of the recorded electrical signal with a built-in reference (Fig. 1b). A key principle is that the test frequency is low in comparison with any sample resonances, yet high enough that a conclusive measurement can be made with reasonable accuracy [10]. The evaluated parameters are presented in Table 2.

TABLE 2

Parameters values of the measured BLT samples

Parameter	BLT0	BLT1	BLT2	BLT3	BLT4	BLT5
$\varepsilon_{33}{}^T$	1301	2330	6703	6917	29277	15423
tanδ	0.0182	0.0329	0.1872	0.2686	0.2136	0.1083
k_{eff}	0.132	0.118	—	—	0.121	0.08
k_p	0.148	0.133	—	—	0.136	0.09
Q_M	218	67	—	—	55	72
d_{33} [pC/N]	84	20	10	3	20	19

- $\varepsilon_{33}{}^T$ – relative permittivity along the poling direction;
- tanδ – dielectric loss tangent;
- k_{eff} – effective electro-mechanical coupling coefficient;
- k_p – planar coupling coefficient;
- Q_M – mechanical quality factor;
- d_{33} – piezoelectric coefficient.

The recorded characteristics of impedance modulus and phase for fundamental resonance frequency range for BLT0 (a), BLT1 (b), BLT2 (c), BLT3 (d), BLT4 (e) and BLT5 (f) with clear tendency of degradation of resonance peaks with increasing lanthanum doping amount in BLT. The alteration of the characteristic parameters of prepared BLT samples with rising La^{3+} concentration at room temperature is referred in Table 2. The static capacitance along the poling direction as well as the relative permittivity rose distinctly together with increasing La^{3+} content for the investigated ceramics and achieve impressing maximal value of $\varepsilon_{33}{}^T$ equal to 29277 for 0.4 mol.% of lanthanum content (Fig. 4). The recorded values of dielectric loss tangent increase with increasing admixture, but it should be emphasized that losses are a relatively small – value of tand does not exceed 0.3. Discussed properties of lanthanum modified BT ceramics are very attractive form applicational point of view – materials with large dielectric permittivity and low value of losses are most desired, especially for use in super capacitors.

Opposite tendency is observed concerning d_{33} piezoelectric coefficient, that has the highest value for basic BT ceramics and continuously drops to the value of 3 pC/N for 0.3 mol.% of lanthanum content (Fig. 4). Such a behavior can be explained considering the fact that high values of permittivity are typical for the ferroelectric soft ceramics, therefore we actually can expect lower values of the piezoelectric coefficients d_{33}.

A similar lowering tendency in material properties of BLT with increasing lanthanum content is partially observed for the recorded values of k_{eff}, k_p and Q_M (Table 2).

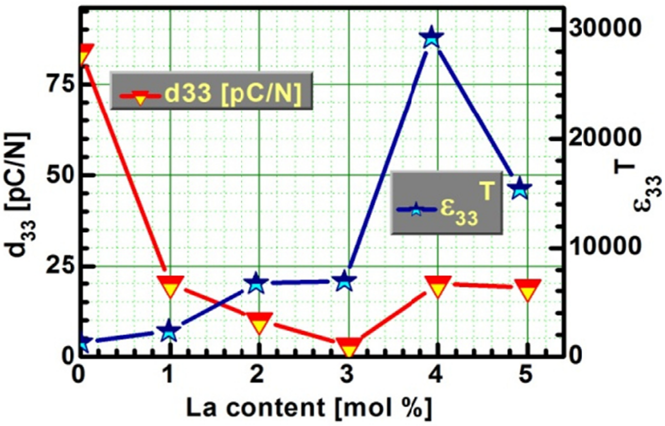


Fig. 4. The variation of the characteristic parameters of prepared BLT samples with raising La^{3+} concentration at room temperature

6. Conclusions

Pure barium titanate ceramics (BT) and La-doped ceramics (BLT), which were prepared by conventional mixed oxide method, exhibit a perovskite-type of structure ABO_3 with tetragonal symmetry P4mm (No. 99). With the increase of lanthanum dopant in $BaTiO_3$ theoretical density increases as well, but the unit cell volume V and tetragonality factor c/a decreases.

The investigation of the piezoelectric coefficients of ceramic samples of $Ba_{1-x}La_xTi_{1-x/4}O_3$ (x = 0, 0.001, 0.002, 0.003, 0.004 and 0.005) were performed. The value of d_{33} piezoelectric coefficient is decreasing with growing amount of lanthanum admixture. The observed tendency is related to the large growth of dielectric permittivity – $\varepsilon_{33}{}^T$ measured at room temperature achieved the value 29277.

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