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FABRICATION AND DIELECTRIC PROPERTIES OF DONOR DOPED BaTiO₃ CERAMICS

OTRZYMYWANIE I WŁAŚCIWOŚCI DIELEKTRYCZNE DONOROWO DOMIESZKOWANEJ CERAMIKI BaTiO₃

Barium titanate BaTiO₃ is a common ferroelectric material which adopts the perovskite structure type ABO₃. It is widely utilized to manufacture a variety of electronic components. In the present study lanthanum-doped BaTiO₃ compositions with $x=0.1$ mol.% and $x=0.3$ mol.%, in Ba_{1-x}La_xTi_{1-x/4}O₃ were prepared by free sintering method in air at temperature $T=1350$ °C. The grain size distribution and morphology of the powders were studied as well as the X-ray diffraction analysis was performed to confirm formation of the desired crystalline structure. Temperature dependence of dielectric permittivity was studied in the temperature range of ferroelectric-paraelectric phase transition.

Keywords: Ba_{1-x}La_xTi_{1-x/4}O₃, donor doped, dielectric permittivity, ferroelectric ceramics

Tytanian baru BaTiO₃ jest przedstawicielem tlenowooktaedrycznych związków o strukturze krystalicznej typu perowskitu ABO₃. Materiał ten charakteryzuje się wieloma interesującymi właściwościami, które można modyfikować poprzez zmianę składu chemicznego oraz optymalizację technologii otrzymywania.

Przedmiotem niniejszej pracy było otrzymanie metodą swobodnego spiekania ($T=1350$ °C) na bazie półprzewodnikowego BaTiO₃, domieszkowanego donorowo lantanem, roztworu stałego o składzie Ba_{1-x}La_xTi_{1-x/4}O₃, dla koncentracji $x=0,1$ mol.% i $x=0,3$ mol.%. Celem zoptymalizowania warunków technologicznych przeprowadzono analizę ziarnową proszków. Wykorzystując metodę dyfrakcji promieni rentgenowskich (metoda XRD) zbadano strukturę krystaliczną, przeprowadzono identyfikację fazową oraz wyznaczono średni wymiar krystalitów otrzymanego roztworu stałego o różnej zawartości lantanu. Zbadano również temperaturowe zależności stałych dielektrycznych w obszarze przemiany fazowej oraz określono parametry ferroelektryczne otrzymanej elektroceramiki.

W wyniku przeprowadzonej pracy wytworzono ceramikę odznaczającą się strukturą typu perowskitu o symetrii tetragonalnej. Stwierdzono, że wzrost koncentracji lantanu w BaTiO₃ powoduje zmniejszenie średniego wymiaru krystalitów, wzrost wartości przenikalności elektrycznej i przesunięcie temperatury przejścia fazowego z fazy ferroelektrycznej do paraelektrycznej w stronę niższych temperatur. Domieszka 0,3 mol.% La powoduje wzrost stopnia rozmycia przemiany fazowej, wzrost stałej Curie i obniżenie temperatury Curie-Weissa.

1. Introduction

Barium titanate (BaTiO₃) is a versatile electroceramics that finds widespread application. At room temperature, BaTiO₃ adopts a tetragonal perovskite type structure and is a ferroelectric with high permittivity. It transforms to the cubic, paraelectric state at the Curie temperature, T_C , of approximates to 130 °C. Undoped BaTiO₃ is electrically insulating, but oxygen deficiency can occur at high temperatures ($T > 350$ °C, in air) and/or in reducing atmospheres [1].

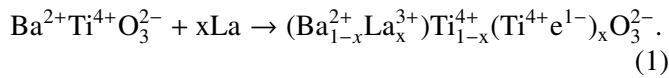
It is known that small additions of lanthanum (<1at.%) induce n-type semiconductivity, which has been widely believed to occur via an electronic compensation mechanism. This phenomenon is commonly

referred to as the lanthanum “donor-doping” mechanism and gives the general formula Ba_{1-x}La_xTiO₃, applicable to compositions where $0.001 \leq x \leq 0.003$. However, in case of the ceramic samples fired under standard conditions lanthanum-doped BaTiO₃ forms primarily according to an ionic, titanium-vacancy compensation mechanism, leading to the general formula Ba_{1-x}La_xTi_{1-x/4}O₃, where $0 \leq x \leq 0.25$ [2].

When pure, this material is highly resistive at room temperature ($\rho > 10^{10}$ Ωcm), but its electrical resistivity can be dramatically lowered by some dopants, like rare earth elements [3-4]. Much lower room-temperature bulk resistivities of the order of $\rho = 10^3 \div 10^5$ Ωcm can be obtained for sintered BaTiO₃ ceramic with 0.1 0.3

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mol.% rare-earth dopants, such as La, Sm and Ce. This is attributed to the occupation of A sites by the La^{3+} (or other rare earth) ions in the perovskite lattice by replacing Ba^{2+} ions. Upon replacement of a Ba^{2+} ion by a La^{3+} ion, an extra positive charge results. Due to the requirement of electrical neutrality, a Ti^{4+} ion must trap an electron (e^{1-}). This can be described as reaction:



To determine the compensation mechanism, a phase diagram study of the ternary system $\text{BaO-La}_2\text{O}_3\text{-TiO}_2$ was required; the locus, or direction, of the solid solutions on the phase diagram found experimentally enabled various plausible compensation mechanisms to be considered, and rejected, since each of these would occur in different regions of the phase diagram [5].

The phase transition temperature decreases with increasing x and, for instance, occurs at about room temperature for $x=0.05$. At the same time, the value of the permittivity at T_C increases and passes through a maximum of approximately $\varepsilon'' = 25000$ at $x=0.06$ and -10°C . With further increase in x , ε'_{max} decreases but also the peak becomes significantly broadened with temperature [6].

Goal of the present research was to fabricate undoped and La-doped BaTiO_3 ceramics, study the influence of La^{3+} doping ions on microstructure, crystalline structure and dielectric properties of BaTiO_3 .

2. Experimental

In the present study pure BaTiO_3 and lanthanum-doped $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$ compositions for $x=0.001$ (0.1 mol.%) and $x=0.003$ (0.3 mol.%) were

prepared by the conventional solid state, mixed-oxide method (MOM). Appropriate amounts of BaCO_3 , La_2O_3 , and TiO_2 (all 99.9 + % purity, Aldrich Chemical Co.) were intimately mixed, with an agate mortar and pestle, until dry, to give the desired composition $\text{Ba}_{0.999}\text{La}_{0.001}\text{Ti}_{0.99975}\text{O}_3$ and $\text{Ba}_{0.997}\text{La}_{0.003}\text{Ti}_{0.99925}\text{O}_3$. Pellets were prepared by pressing powders to 300 MPa in 10 mm diameter stainless-steel die. The green bodies were placed in an alumina crucible, and fired in air at temperature $T_S=950^\circ\text{C}$, $t=2\text{h}$ (synthesis) and $T_1=1250^\circ\text{C}$, $T_2=1300^\circ\text{C}$, $T_3=1350^\circ\text{C}$ for 2h (free sintering method), with heating and cooling rates of 5°Cmin^{-1} . All the samples were furnace-cooled to room temperature.

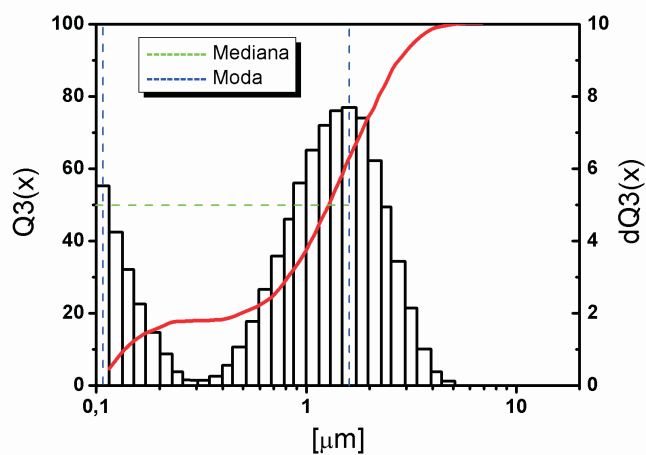
The grain size distribution of the initial powders was measured with an Analysette 22 Comfort equipment.

The crystal structure was studied by X-ray diffractometer (XRD, Philips PW 3710, $\text{CoK}\alpha_1$ radiation, $\Theta - 2\Theta$ method, data angle range $2\Theta=10-90^\circ$, scan step size $\Delta 2\Theta=0.01$, scan step time $t=8\text{ s}$, $\lambda=1.789007\text{ \AA}$). For electrical measurements the end surface electrodes were prepared using conducting silver paste. The dielectric properties were determined with the bridge technique utilizing the automatic RLC bridge BM595 (Tesla) for both heating and cooling under the influence at weak electric field ($E \sim 50\text{ V/m}$). Temperature dependence of the real part of dielectric permittivity was measured from $T=20^\circ\text{C}$ to $T=250^\circ\text{C}$.

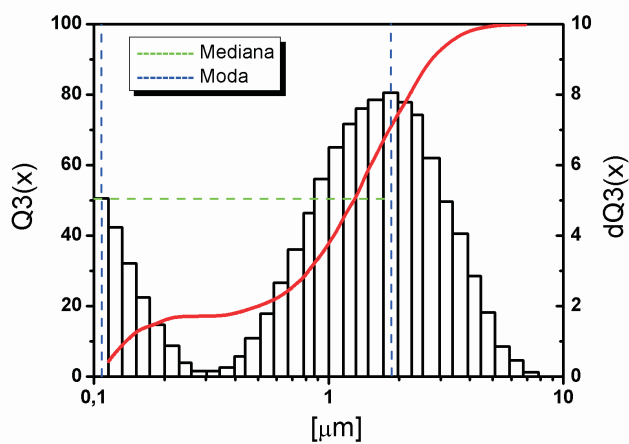
3. Results and discussion

Results of the grain size distribution of the powders used for ceramics fabrication are given in Fig. 1. One can see that the powders exhibit small particle size with mode and median less than $2\text{ }\mu\text{m}$.

a)



b)



c)

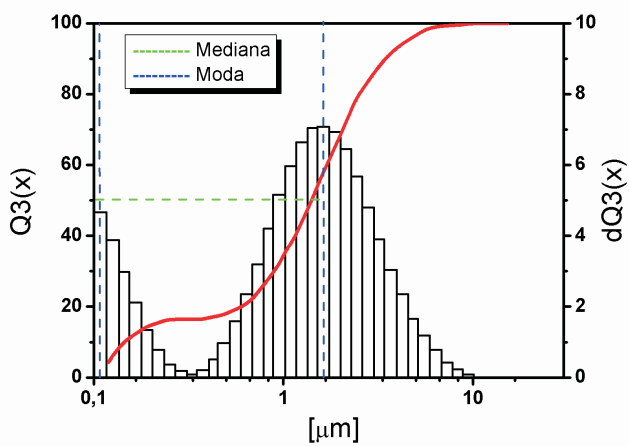


Fig. 1. Characterization of the powders grains size distribution for: BaTiO_3 (a), $\text{BaTiO}_3 + 0.1 \text{ mol.\% La}$ (b), $\text{BaTiO}_3 + 0.3 \text{ mol.\% La}$ (c)

The X-ray diffraction analysis confirmed formation of the desired crystalline structure. A careful examination of the XRD reflection intensities further indicates that no preferred orientation could be found for any sample. The lattice parameters for BaTiO₃ and Ba_{1-x}La_xTi_{1-x/4}O₃ were calculated for tetragonal phase

using the Rietveld refinement [7], embedded into the computer programme PowderCell 2.4.

A model structure used for diffraction pattern fitting exhibited space group *P4mm* (SG number: 99) (Fig. 2), detailed information about the model structure used is given in Tab. 1 whereas the details of calculated X-ray spectra are given in Tab. 2.

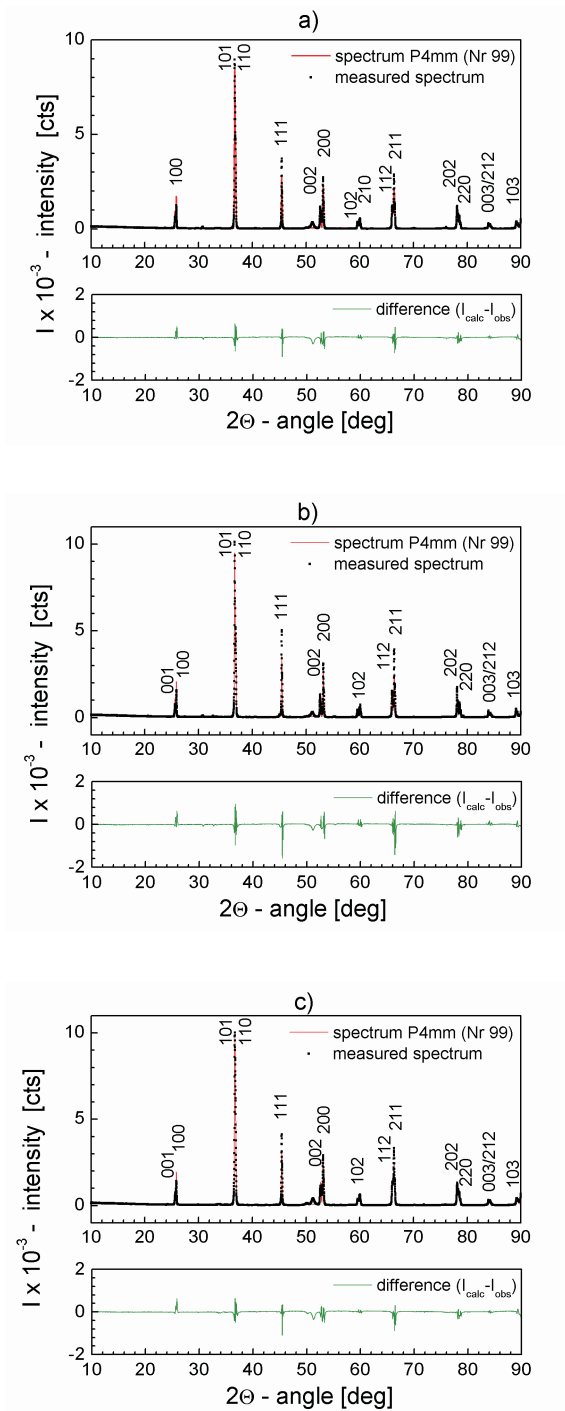


Fig. 2. X-ray diffraction patterns for pure BaTiO₃ (a), BaTiO₃+0.1 mol.% La (b) and 0.3 mol.% La (c)

TABLE 1

Parameters of the model structure used for the XRD pattern fitting for pure BaTiO₃ (a), BaTiO₃+0.1 mol.% La (b) and 0.3 mol.% La (c) (see Fig. 5). The following parameters are given: *Z* – atomic mass number, *Wyck.* – Wyckoff positions, *x, y, z,* – relative atomic coordinates, *SOF* – site occupation factor, *B* – Debye-Waller factor

a)

Space group number	99
Space group	P 4 m m
Cell choice	1
Lattice parameter	3.9945 Å 3.9945 Å; 4.0296 Å
Angles	90.0000° 90.0000° 90.0000°
Atoms in asymmetric unit	4
Atoms in unit cell	5.0, 5 generated positions
Volume of cell	64.30 Å ³
Relative mass of unit cell	233.24
X-ray density	6.0237 g/cm ³
Mass absorpt. coef.	338.02 cm ⁻¹ /g

Name	Z	Ion	Wyck.	x	y	z	SOF	B
Ba1	56	Ba ²⁺	1a	0.0000	0.0000	1.0000	1.0000	0.0000
Ti1	22	Ti ⁴⁺	1b	0.5000	0.5000	0.5274	1.0000	0.5427
O1	8	O ²⁻	1b	0.5000	0.5000	0.9993	1.0000	0.0000
O2	8	O ²⁻	2c	0.5000	0.0000	0.5125	1.0000	0.0000

b)

Space group number	99
Space group	P 4 m m
Cell choice	1
Lattice parameter	3.9922 Å 3.9922 Å 4.0329 Å
Angles	90.0000° 90.0000° 90.0000°
Atoms in asymmetric unit	4
Atoms in unit cell	5.0, 5 generated positions
Volume of cell	64.36 Å ³
Relative mass of unit cell	232.79
X-ray density	6.0062 g/cm ³
Mass absorpt. coef.	338.68 cm ⁻¹ /g

Name	Z.No.	Ion	Wyck.	x	y	z	SOF	B
Ba1	56	Ba ²⁺	1a	0.0000	0.0000	1.0000	1.0000	0.0000
Ti1	22	Ti ⁴⁺	1b	0.5000	0.5000	0.5142	0.9906	2.0950
O1	8	O ²⁻	1b	0.5000	0.5000	0.9745	1.0000	0.6422
O2	8	O ²⁻	2c	0.5000	0.0000	0.4877	1.0000	0.0000

c)

Space group number	99
Space group	P 4 m m
Cell choice	1
Lattice parameter	3.9961 Å 3.9961 Å 4.0276 Å
Angles	90.0000° 90.0000° 90.0000°
Atoms in asymmetric unit	4
Atoms in unit cell	5.0, 5 generated positions
Volume of cell	64.36 Å ³
Relative mass of unit cell	233.14
X-ray density	6.0154 g/cm ³
Mass absorpt. coef.	338.16 cm ⁻¹ /g

Name	Z.No.	Ion	Wyck.	x	y	z	SOF	B
Ba1	56	Ba ²⁺	1a	0.0000	0.0000	1.0000	0.9999	0.0000
Ti1	22	Ti ⁴⁺	1b	0.5000	0.5000	0.5142	0.9983	0.7573
O1	8	O ²⁻	1b	0.5000	0.5000	0.9745	1.0000	0.3281
O2	8	O ²⁻	2c	0.5000	0.0000	0.4877	1.0000	0.0000

Details of calculated X-ray diffraction pattern for pure BaTiO₃ (a), BaTiO₃+0.1 mol.% La (b) and 0.3 mol.% La (c) (see Fig. 4). The following parameters are given: d_{hkl} – Miller indices, 2Θ – diffraction angle, d_{hkl} – interplanar distance, I – relative intensity, $|F(hkl)|$ – the structure factor, Mu – multiplicity, $FWHM$ – Full Width at Half Maximum

Source X-ray Co-K α_1 1.789007 Å
 2Θ 10.005° – 89.995°
 Geometry Bragg-Brentano + monochr., fixed slit, anomalous dispersion

a)

h	k	l	$2\Theta[deg]$	$d_{hkl}[\text{Å}]$	$I[rel.]$	$ F(hkl) $	Mu	$FWHM$
1	0	0	25.651	4.0296	8.78	22.37	1	0.138
1	0	1	36.76	2.83687	100	55.1	4	0.1575
1	1	0	36.926	2.82454	98.39	54.92	4	0.1578
1	1	1	45.504	2.31292	38.18	42.81	4	0.1767
0	0	2	52.714	2.0148	17.71	68.31	1	0.1951
2	0	0	53.214	1.99725	69.29	68.24	4	0.1965
1	0	2	59.636	1.79892	5.23	21.14	4	0.215
2	1	0	60.097	1.78639	10.11	20.96	8	0.2164
1	1	2	66.096	1.64026	19.22	44.99	4	0.2357
2	1	1	66.423	1.63311	38.84	45.44	8	0.2368
2	0	2	78.193	1.41843	22.04	55.9	4	0.2808
2	2	0	78.6	1.41227	21.86	55.88	4	0.2825
0	0	3	83.51	1.3432	0.7	20.89	1	0.3037
2	1	2	84.012	1.33666	5.19	20.15	8	0.306
1	0	3	89.271	1.27315	9.49	39.73	4	0.3313

b)

h	k	l	$2\Theta[deg]$	$d_{hkl}[\text{Å}]$	$I[rel.]$	$ F(hkl) $	Mu	$FWHM$
1	0	0	25.896	3.9922	38.7	23.5	4	0.1369
1	0	1	36.755	2.83719	100	54.6	4	0.1506
1	1	0	36.948	2.82291	96.25	53.86	4	0.1509
1	1	1	45.509	2.31265	39.7	43.26	4	0.1649
0	0	2	52.668	2.01645	16.84	65.94	1	0.1787
2	0	0	53.247	1.9961	67.11	66.6	4	0.1799
1	0	2	59.601	1.79988	6.41	23.18	4	0.194
2	1	0	60.135	1.78537	12.11	22.74	8	0.1953
1	1	2	66.07	1.64083	18.26	43.44	4	0.2102
2	1	1	66.449	1.63254	37.19	44.08	8	0.2112
2	0	2	78.182	1.4186	20.14	52.94	4	0.2459
2	2	0	78.654	1.41146	20.41	53.53	4	0.2475
0	0	3	83.427	1.3443	0.77	21.71	1	0.2641
2	1	2	84.008	1.33671	6.75	22.76	8	0.2662
1	0	3	89.194	1.27401	9.32	38.99	4	0.2863

c)

h	k	l	$2\Theta[deg]$	$d_{hkl}[\text{Å}]$	$I[rel.]$	$ F(hkl) $	Mu	$FWHM$
1	0	0	25.87	3.9961	36.69	22.96	4	0.1535
1	0	1	36.761	2.83674	100	55.32	4	0.1699
1	1	0	36.91	2.82567	96.96	54.72	4	0.1702
1	1	1	45.499	2.31316	36.36	42.32	4	0.1869
0	0	2	52.743	2.0138	16.37	67.17	1	0.2034
2	0	0	53.191	1.99805	65.72	67.94	4	0.2045
1	0	2	59.656	1.79835	5.18	21.72	4	0.2214
2	1	0	60.07	1.78711	9.81	21.29	8	0.2226
1	1	2	66.111	1.63994	17.78	45.04	4	0.2404
2	1	1	66.404	1.63352	35.96	45.51	8	0.2413
2	0	2	78.197	1.41837	19.01	54.77	4	0.2822
2	2	0	78.562	1.41283	19.33	55.44	4	0.2837
0	0	3	83.561	1.34253	0.57	19.99	1	0.304
2	1	2	84.011	1.33667	4.94	20.81	8	0.3059
1	0	3	89.317	1.27263	8.88	40.77	4	0.3299

R -values of the Rietveld analysis obtained under assumption of $P4mm$ space group (setting 1) are as follows: $R_p=23.65\%$, $R_{wp}=37.58\%$, $Re=13.88\%$ (pure $BaTiO_3$), $R_p=26.61\%$, $R_{wp}=38.88\%$, $Re=11.22\%$ (for 0.1 mol.% La), $R_p=23.92\%$, $R_{wp}=40.33\%$, $Re=11.72\%$ (for 0.3 mol.% La). For fitting the diffraction profile the pseudoVoigt2 function was used and the following uvw parameters. Although numerical criteria of goodness of fit (i.e. R -values) are very important, it is necessary to point out that they do not fully reflect the quality of fitting. Graphical criteria such as plots of the calculated and observed intensities as well as a plot of the difference between the calculated and observed intensities are also necessary. From the trace on the bottom of Fig. 2 one can see that there are no gross errors of fitting coming from bad scaling parameters, or incorrect crystalline structure used for simulation, or incorrect unit cell parameters.

The calculated unit cell parameter for supposed tetragonal symmetry space group $P4mm$ were as follows: pure $BaTiO_3$ ceramics: $a_0=0.39945$ nm, $c_0=0.40296$ nm and 0.1 mol.% La doped $BaTiO_3$ ceramics: $a_0=0.39922$

nm, $c_0=0.40329$ nm and 0.3 mol.% La doped $BaTiO_3$ ceramics: $a_0=0.39961$ nm, $c_0=0.40276$ nm. It follows from the X-ray diffraction the volume of the elementary cell increased from $V=64.30 \times 10^{-30}$ m³ (pure $BaTiO_3$) to $V=64.36 \times 10^{-30}$ m³ (doped $BaTiO_3$ + 0.1 and 0.3 mol.% La).

To calculate the mean crystallite size the approximation method was used, utilizing the full width at half maximum of the six diffraction lines fitted with Gaussian function and based on the Scherrer's equation:

$$D = K\lambda/(\beta \cos\Theta), \quad (2)$$

where:

D – mean crystallite size;

K – Scherrer's constant;

λ – X-diffraction wavelength;

β – FWHM.

The dependence of β^2 on $\sin^2\Theta$ given in Fig. 3 helps to determine contribution of the mean crystallite size in to FWHM.

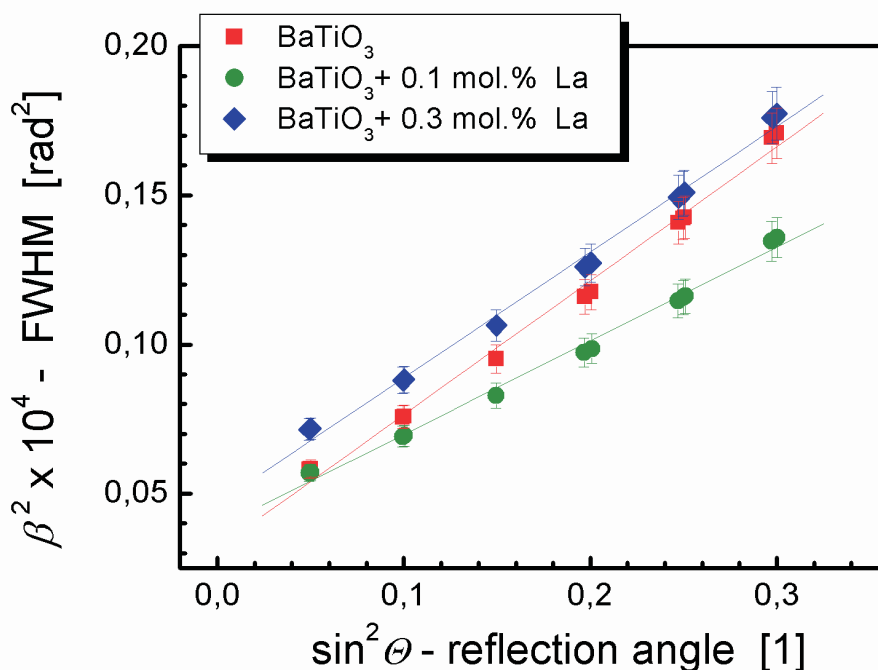


Fig. 3. FWHM vs. $\sin^2\Theta$ for pure $BaTiO_3$, and doped $BaTiO_3$ + 0.1 and 0.3 mol.% La

Results of the calculations have shown that the mean crystallite size for pure $BaTiO_3$ ceramics is $D_1=40$ nm, whereas to 0.1 mol.% doped $D_2=36$ nm and for 0.3 mol.% doped $D_3=33$ nm.

Study at dielectric properties, i.e. – measurement the dielectric permittivity (ϵ') and dielectric loss tan-

gents ($\text{tg}\delta$) were performed. Dielectric losses in a form of imaginary part of dielectric permittivity (ϵ'') are given in Fig. 4b, 5b.

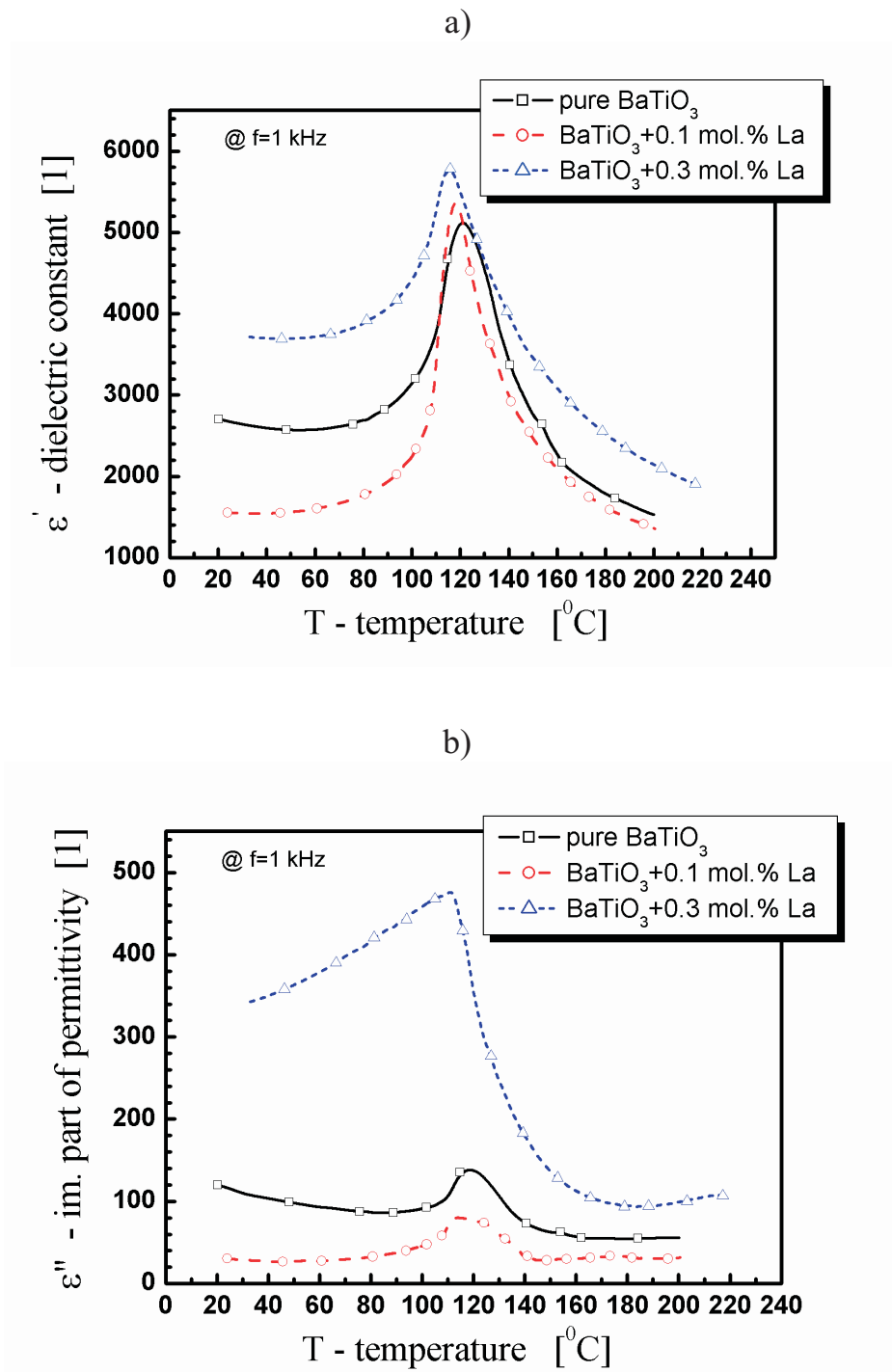


Fig. 4. Dielectric constant ϵ' (a) and ϵ'' (b) at 1 kHz as a function of temperature of BT, BLT + 0.1 and 0.3 mol.% La

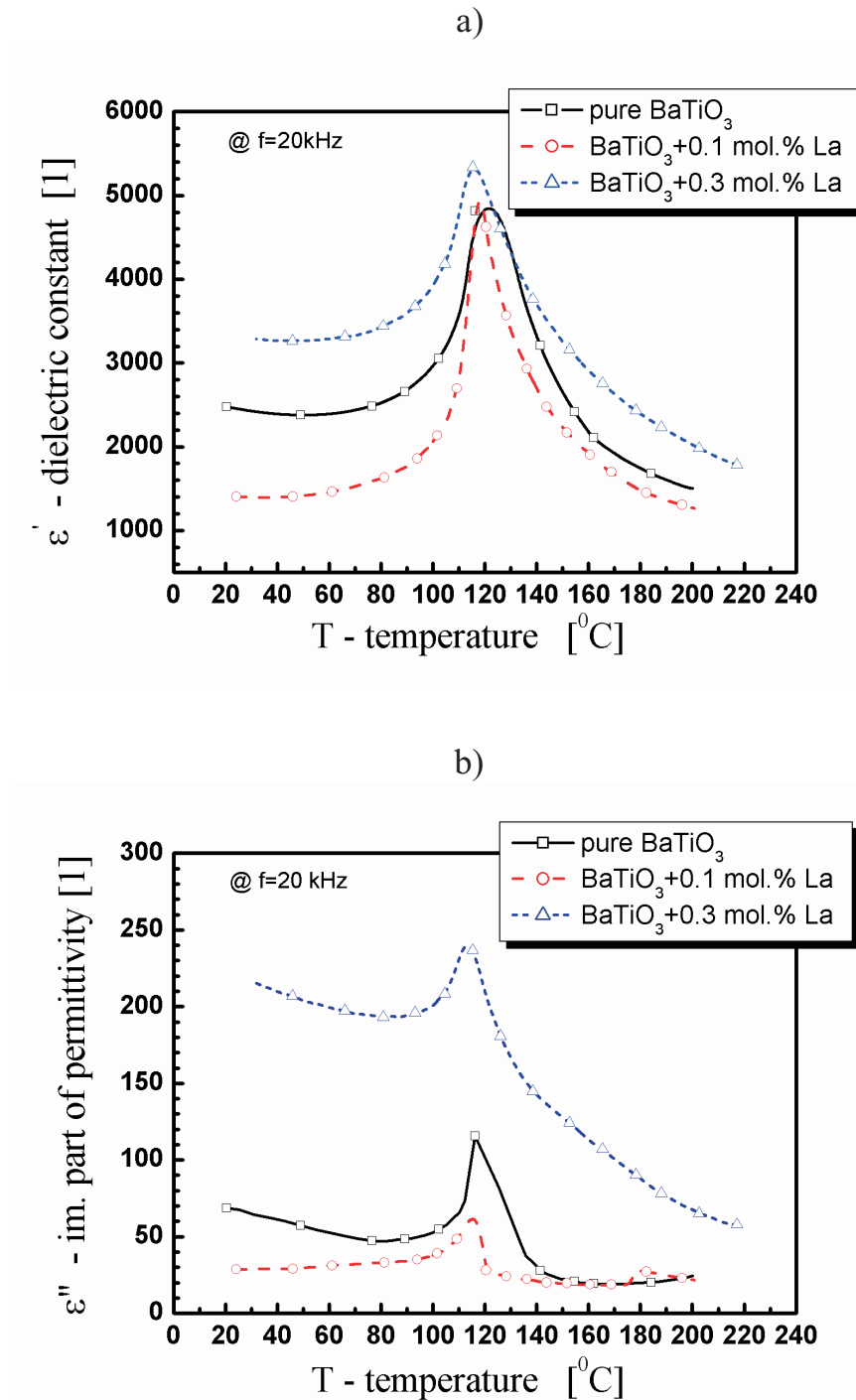


Fig. 5. Dielectric constant ε' (a) and ε'' (b) at 20 kHz as a function of temperature of BT, BLT + 0.1 and 0.3 mol.% La

One can see from Fig. 4a that with an increase in lanthanum dopant ε'_{max} increases and the Curie point shifts towards lower temperatures. On the other side the temperature dependence of ε'' shows that small amount of La can cause either a decrease in dielectric loss (0.1 mol.%) or an increase (0.3 mol.%). The characteristic given in Fig. 4 were performed at frequency of the measuring field $\nu=1\text{kHz}$. The similar results have been ob-

tained for the higher frequency of the measuring field ($\nu=20\text{kHz}$). One can see from Fig. 5 that both real and imaginary part of the dielectric permittivity have decreased with an increase of frequency what proves the low frequency dispersion of ceramics.

On the base of analysis of the $1/\varepsilon(T)$ dependence (Fig. 6) the diffuseness of the phase transition was determined as a function of content of La^{3+} dopant.

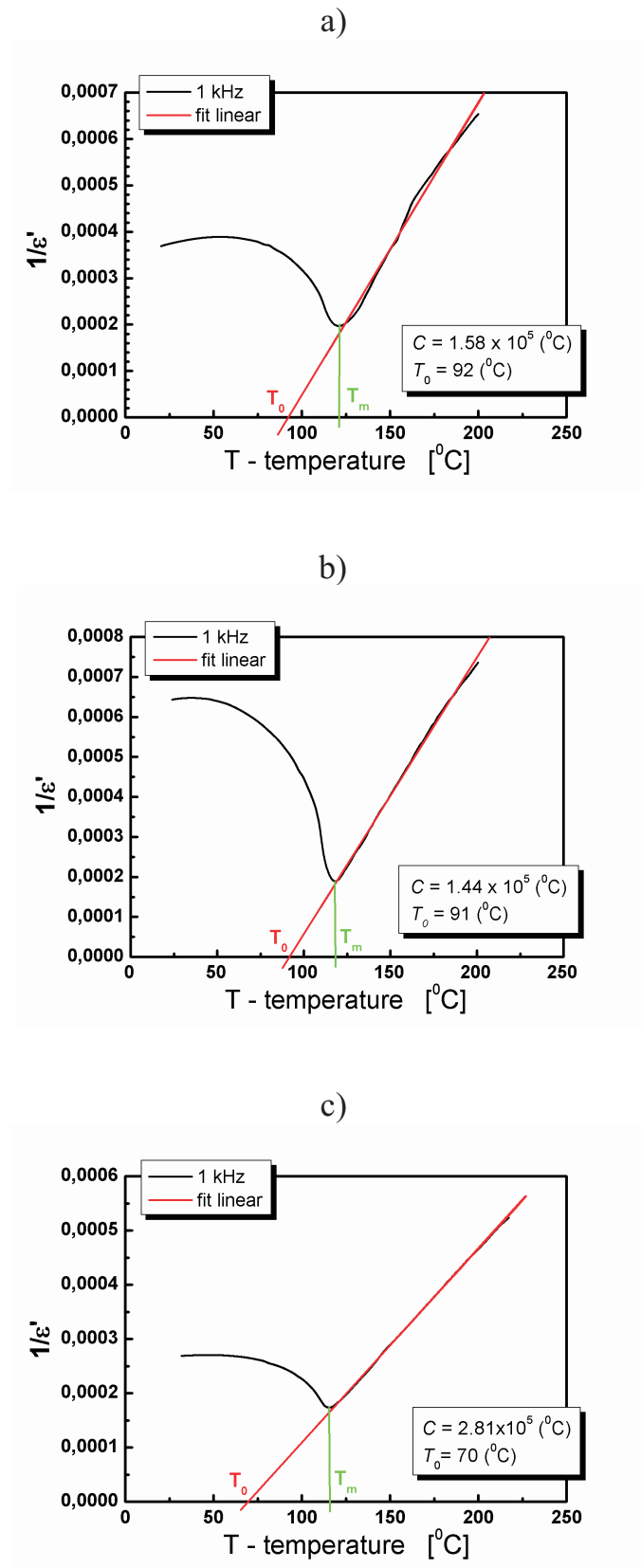


Fig. 6. The reciprocal permittivity ($1/\epsilon'$) at 1kHz as a function of temperature for: BaTiO_3 ceramic (a), $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ ceramic where $x=0.1$ mol.% (b) and $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ ceramic where $x=0.3$ mol.% (c)

Dielectric properties were also studied in both temperature and frequency domains and the values of the Curie-Weiss temperature (T_0), Curie temperature (T_m)

and the Curie constant (C) were also calculated. The abovementioned parameters of the phase transition are given in Tab.3.

TABLE 3
Ferroelectric parameters (peak permittivity ε'_{max} , dielectric loss tangent $\text{tg}\delta$, Curie temperature T_C , Curie-Weiss temperature T_0 and order parameter fluctuations ($T_C - T_0$) of BaTiO_3 and $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ for $x=0.1$ and 0.3 mol.% at 1kHz

Sample	ε'_{max}	$\text{tg}\delta$	C ($^{\circ}\text{C}$)	T_C ($^{\circ}\text{C}$)	T_0 ($^{\circ}\text{C}$)	$T_C - T_0$ ($^{\circ}\text{C}$)
BaTiO_3	5415	0.0265	1.58×10^5	121	92	29
$\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ $x=0.1$ mol. %	5781	0.0181	1.44×10^5	118	91	27
$\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ $x=0.3$ mol. %	5783	0.0742	2.81×10^5	115	70	45

4. Conclusions

In the present research both doped and La^{3+} - doped BaTiO_3 ceramics exhibiting a perovskite - type structure with tetragonal symmetry were fabricated by MOM followed by 3-step sintering process. It was found that increase in La^{3+} concentration causes: a decrease in mean dimension of crystallites from $D_1=40$ nm (pure BaTiO_3) to $D_3=33$ nm (BaTiO_3 with 0.3 mol.% La); an increase in volume at the elementary cell BaTiO_3 ceramics from $V=64.30 \times 10^{-30}$ m³ (pure BaTiO_3) to $V=64.36 \times 10^{-30}$ m³ (BaTiO_3 with 0.1 i 0.3 mol.% La) and an increase in dielectric permittivity and shift of the temperature of the ferroelectric-paraelectric phase transition towards lower temperatures.

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