Properties of lanthanum doped BaTiO$_3$ produced from nanopowders

M.M. Vijatović [a,*], B.D. Stojanović [a], J.D. Bobić [a], T. Ramoska [b], P. Bowen [c]

[a] Institute for Multidisciplinary Research, Belgrade University, Kneza Višeslava 1, 11000 Belgrade, Serbia
[b] Faculty of Physics, Vilnius University, Sauletekio al. 9, Vilnius, Lithuania
[c] Ecole Polytechnique Fédérale de Lausanne, Station 12, 1015 Lausanne, Switzerland

Abstract

Pure and barium titanate (BT) powders doped with different lanthanum concentration were prepared by the polymeric precursor method (Pechini process) which was carried out as a three-stage process from organometallic complexes. Sintering of pressed powders was performed at 1300 °C for 2, 4 and 8 h. XRD analysis showed cubic BT powders with crystallite sizes between 20 and 25 nm and tetragonal crystal structure of BT ceramics. The influence of sintering time on grain growth was fairly obvious. It was found that lanthanum doping has significant effect on powders particle size and ceramics grain size. The influence of lanthanum concentration on grain size inhibition, improving the dielectric properties of BT ceramics was detected. The relation between sintering time, grain size, structure and electrical properties of the BT ceramics was analyzed.

1. Introduction

Since the discovery of ferroelectricity intensive research in the sphere of polycrystalline ceramics has lead to great technological progress and success in the field of ferroelectric materials. Ferroelectric perovskites belong to large group of ferroelectric materials and they have very important role due to its wide application in electronics. Barium titanate has a special place in this group of compounds because it can be formulated in a large number of systems and solid solutions that provide a wide range of various applications. The perovskite structure has capability to host ions of different size, so a large number of different dopants can be accommodated in the BaTiO$_3$ lattice which makes BaTiO$_3$ semiconducting. Doping of BaTiO$_3$ (BT) ceramics is very important to obtain required characteristics for different applications. For many years, A- and B-site dopants have been used to modify the electrical properties of BaTiO$_3$. It is well known that semiconducting barium titanate can be produced by atmospheric reduction (forming oxygen vacancies) or by donor doping with trivalent ions (lanthanum, yttrium, antimony) on Ba-ion sites, or with heptavalent ions (niobium, antimony, tantalum) on Ti-ion sites [1]. Concentration of donor or acceptor dopants is very low therefore barium titanate purity has to be high as well as the control of each process step. Ionic radius is main parameter that determines the substitution site. La^{3+} (1.15 Å) is exclusively incorporated at the Ba^{2+} (1.35 Å) site, as its size is incompatible with that of Ti^{4+} (0.68 Å), La^{3+} produces n-type semiconductors. Addition of lanthanum as a donor dopant at a relatively low concentration (<0.5 at%) leads to room temperature semiconducting ceramics with positive coefficient of resistivity (PTCR) properties, whereas higher dopant concentration leads to insulating materials [2,3].

The literature data mainly reports the preparation of lanthanum doped BT by solid state reaction [3–6]. Among the several soft chemistry routes that can be used, the polymeric precursor method has the advantage of assuring chemical purity of the final product what is very important for final properties of obtained material.

Thus, in this work the influence of lanthanum doping on properties of barium titanate powders and ceramics prepared from polymeric precursor method was studied. Effect of lanthanum on microstructure and morphology of barium titanate were monitored and electrical properties were investigated.

* Corresponding author. Tel.: +381 11 2085039; fax: +381 11 2085062.
E-mail address: miravijat@yahoo.com (M.M. Vijatović).

Table 1
Results for pure and doped barium titanate powders.

Sample	D_{V50} (nm)	SSA (m^2/g)	D_{BET} (nm)	F_{agg}	Density (g/cm^3)	D_{SEM} (nm)	D_{XRD} (nm)
BT	6530	13.47	74.07	88.16	5.7186	40	20–23
BTL1	7080	10.98	90.85	77.93	5.7388	40	22–24
BTL3	7820	13.48	74.00	105.68	5.7172	30	20–24
BTL5	12570	10.86	91.85	136.85	5.7215	25	20–23

2. Experimental

Barium titanate (BaTiO$_3$-BT) powders were prepared by the polymeric precursor method (Pechini process-PPM) starting from barium and titanium citrates. Firstly, titanium citrate and barium citrate solutions were prepared, using titanium iso-propoxide (Ti[OCH(CH$_3$)$_2$]$_4$, Alfa Aesar, 99.995%) and barium acetate (Ba(CH$_3$COO)$_2$, Alfa Aesar, 99.0–102.0%). The molar ratio of citric acid to ethylene glycol was 4:16, for both citrate solutions. Solutions of titanium citrate and barium citrate were mixed, with constant stirring until it became a clear transparent yellow solution. For doping barium titanate, lanthanum nitrate hexahydrate solution was added (La(NO$_3$)$_3$·6H$_2$O, Alfa Aesar, 99.99%) with 0.1, 0.3 and 0.5 mol% La (BTL1, BTL3 and BTL5). Temperature was raised to 120–140 °C, to promote polymerization and remove solvents. The solution became more viscous and changed color from yellow to brown and finally solution solidifies into a dark-brown glassy resin [7]. 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, the heating rate was 2 °C/min. The resin became a black solid mass and material was pulverized, using Agate Mortar and pestle, before further treatment. Thermal treatment was performed at 500 °C for 4 h, 700 °C for 4 h and 800 °C for 2 h. The agglomerates were broken in agate pulverizer (Fritisch Pulverisette, Type 02.102). After drying at room temperature and passing through sieve (200 mesh), the barium titanate powder was obtained [8].

The powders were isostatically pressed into pellets 8 mm in diameter and average thickness of about 2.5 mm at pressure of 98.1 MPa. Sintering was performed at 1300 °C for 2, 4 and 8 h (in a tube furnace "Lenton", UK) and the heating rate was 10 °C/min with nature cooling in an air atmosphere.

Particle size distributions (PSDs) were measured using laser diffraction (Malvern Mastersizer S) and specific surface areas (SSA) were determined by nitrogen adsorption (Gemini 2375, Micromeritics). The average particle diameters (D_{BET}) were calculated from the SSA ($6/(\rho_{\text{theoretical}} \times \text{SSA})$) as well as
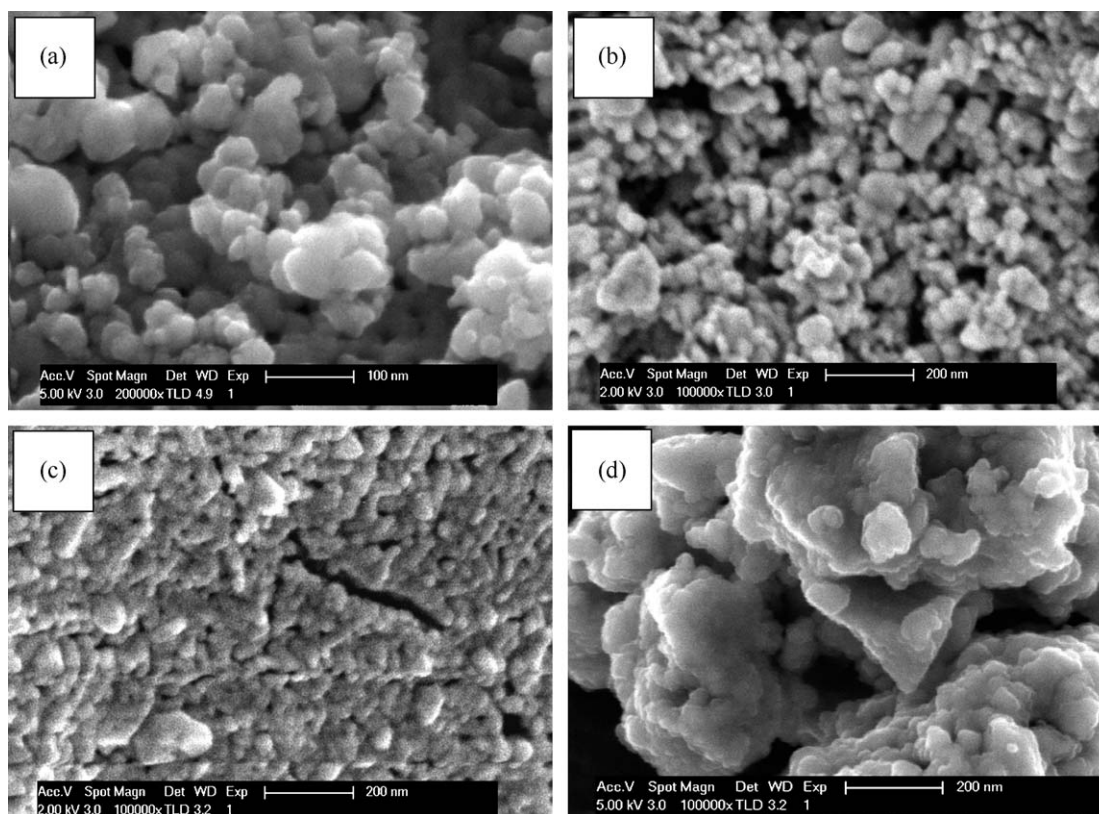

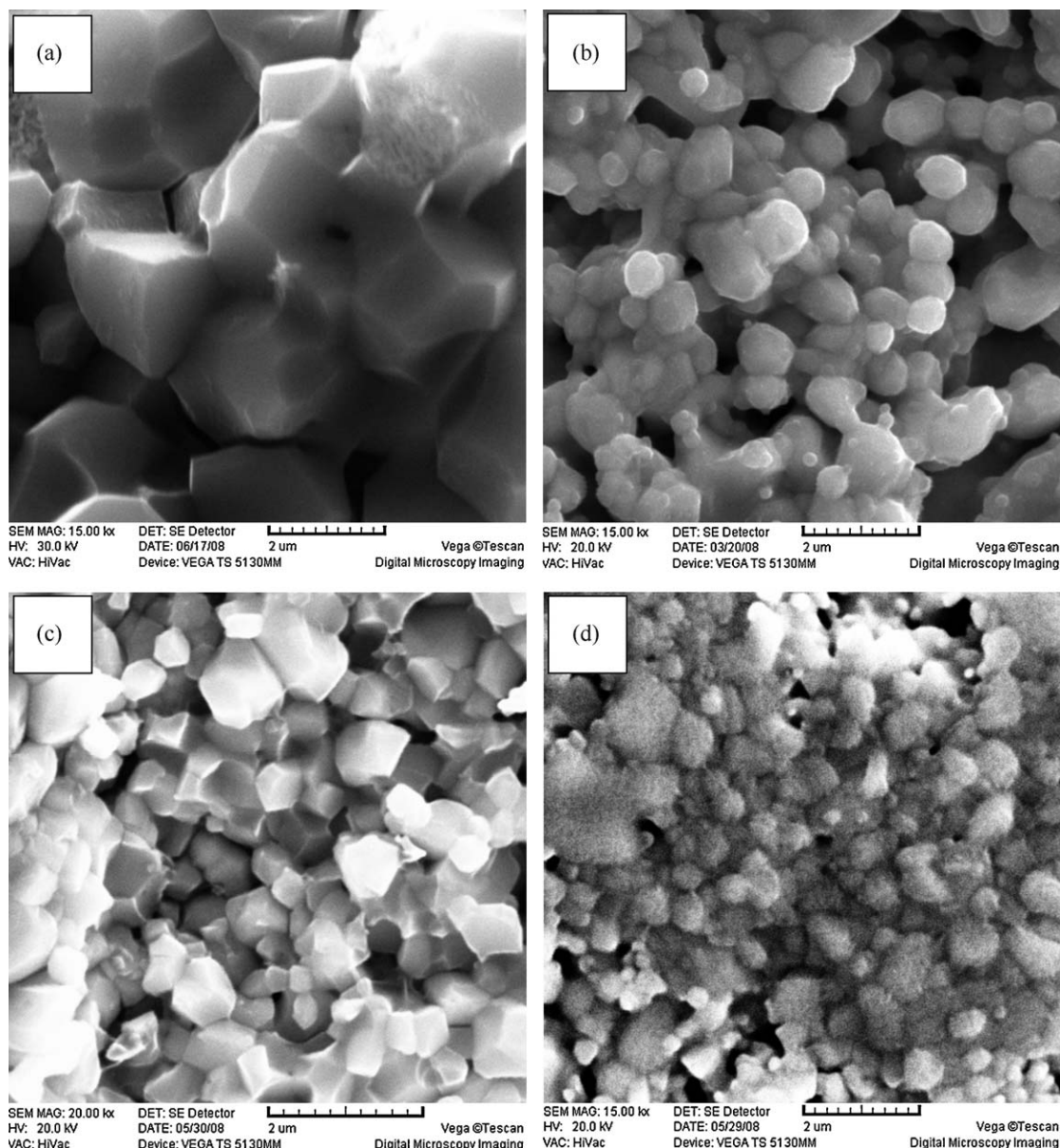Fig. 1. SEM photographs of (a) BT, (b) BTL1, (c) BTL3 and (d) BTL5 barium titanate powders.

Fig. 2. Micrographs of barium titanate specimens sintered at 1300 °C for 2 h BT, (b) BTL1, (c) BTL3 and (d) BTL5.

agglomeration factor, F_{agg} by dividing the D_{V50} with the D_{BET}. Density of pure and doped barium titanate powders was measured using a He Pycnometer (Micromeritics AccuPyc 1330) and density of barium titanate ceramics was obtained by measuring dimensions of the samples and calculating from equation $\rho = 4 \cdot m/d^2 \cdot h \cdot \pi$ (where m is the mass, d is the average diameter and h is the height of the sintered samples). The microstructure and morphology of nanopowders and sintered samples were investigated using X-ray diffraction (Model Phillips PW1710 diffractometer) and scanning electron microscope (Tescan VEGA TS 5130MM). The microstructure of sintered samples was obtained by polishing and thermally etching during 30 min at 1200 °C and some of the samples were observed at fracture surface. Dielectric measurements were carried out using an LCR meter (model 4284 A, Hewllet-Packard).

3. Results and discussion

The XRD results of all powders indicate the formation of well crystallized cubic phase of $BaTiO_3$ (identified using the JCPDS files no. 31-0174) with crystallite size of about 20–24 nm. Experimental results are shown in Table 1.

It can be concluded that powders of barium titanate obtained by polymeric precursor method are nanosized, but particle size distribution measurement pointed that the powders are highly agglomerated which can be also seen from calculated agglomeration factor (Table 1). Densities of all powders have almost the same value 5.72 ± 0.02 [9].

Fig. 1 shows the SEM photographs of the $BaTiO_3$ powders. SEM observation indicates that concentration of La has effect on primary particle size. The primary particles in BT and BTL1 powders have rounded shape with uniform size ~40 nm. The
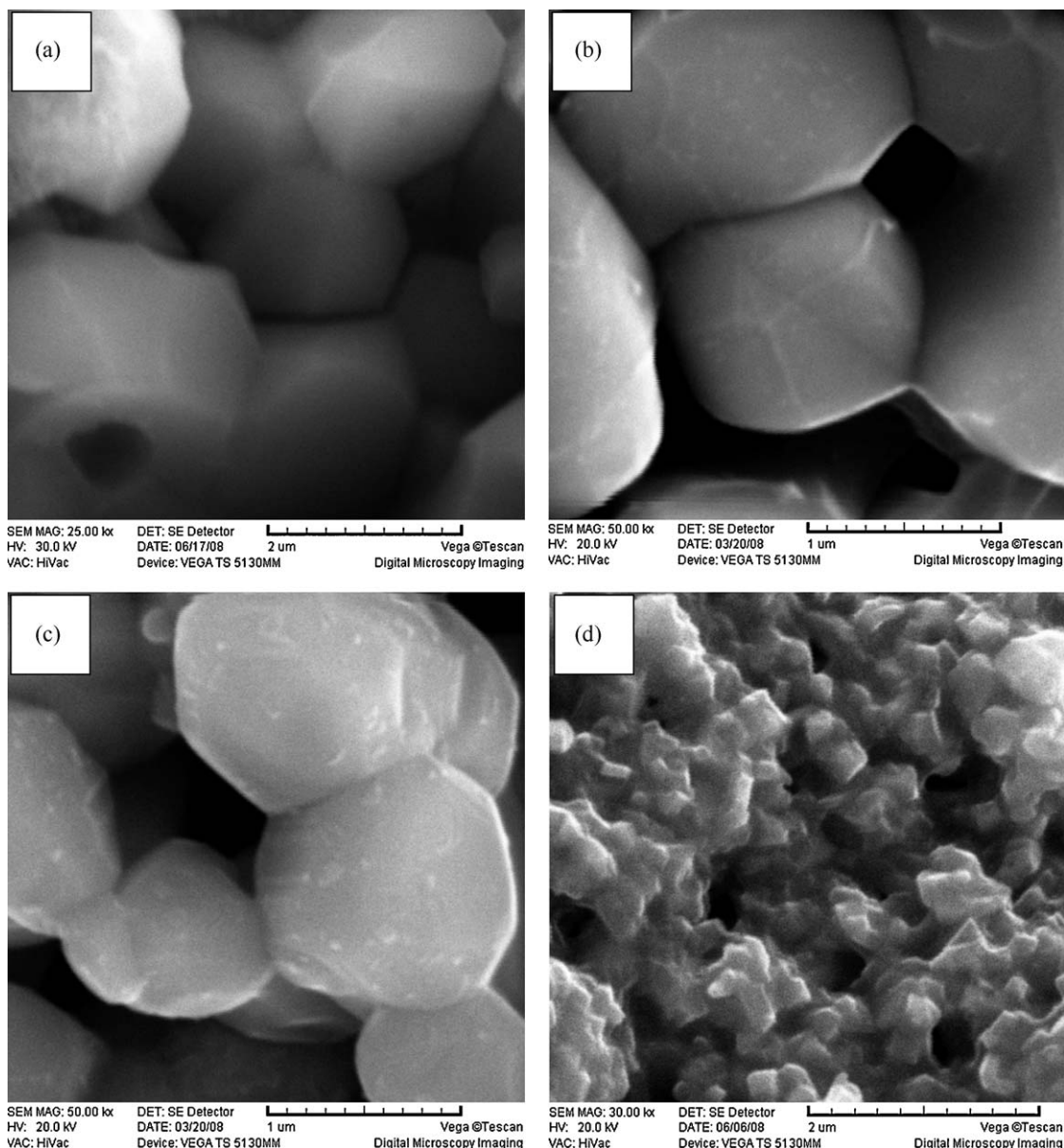
Fig. 3. Micrographs of barium titanate specimens sintered at 1300 °C for 4 h BT, (b) BTL1, (c) BTL3 and (d) BTL5.

particle size of about 30 nm was obtained for barium titanate powder BTL3 and 25 nm for BTL5 powder. It can be assumed that very low concentration of lanthanum has no influence on particle size compared to BT powders. Meanwhile, the particle size decreases with increasing dopant concentration, also reported by other authors for sol–gel methods [10].

The XRD results of sintered samples for different dopant concentration and sintering time show the formation of well crystallized tetragonal phase of BaTiO$_3$ (identified using the JCPDS files no. 05-0626) [11]. However, it was observed that samples of doped barium titanate possess different colors after sintering, from pale yellow for BTL1 samples, to light grey for BTL3 samples and dark grey for BTL5 samples. This is an indication that the material is being reduced and turning to n-type semiconductor [12,13].

Figs. 2–4 show microstructure of barium titanate ceramics sintered at 1300 °C for various sintering times, 2, 4 and 8 h,

respectively. The average grain size and density of pure and doped BaTiO$_3$ ceramics are reported in Table 2.

It is well known that it is difficult to prepare fully dense nanostructured ceramics due to a lot of factors which can affect on producing fine-grained materials with high density. Strong influence has the powder preparation process and powder agglomeration, as well as sintering regime (sintering temperature, time and atmosphere) [14]. Dopants can also have effect on the densification and microstructure of barium titanate [15]. Obtained microstructures reveal that the relatively short time of sintering is not enough for significant grain growth. The prolongation of sintering time increases the densification and grain growth [16]. The highest densities were observed in the pure BT ceramics sintered for 8 h. It was observed that pure BT has higher value of density compared to lanthanum doped BT (Table 2). The difference in grain size for BTL1 and BTL3 samples is small after 2 h sintering. The average grain size is
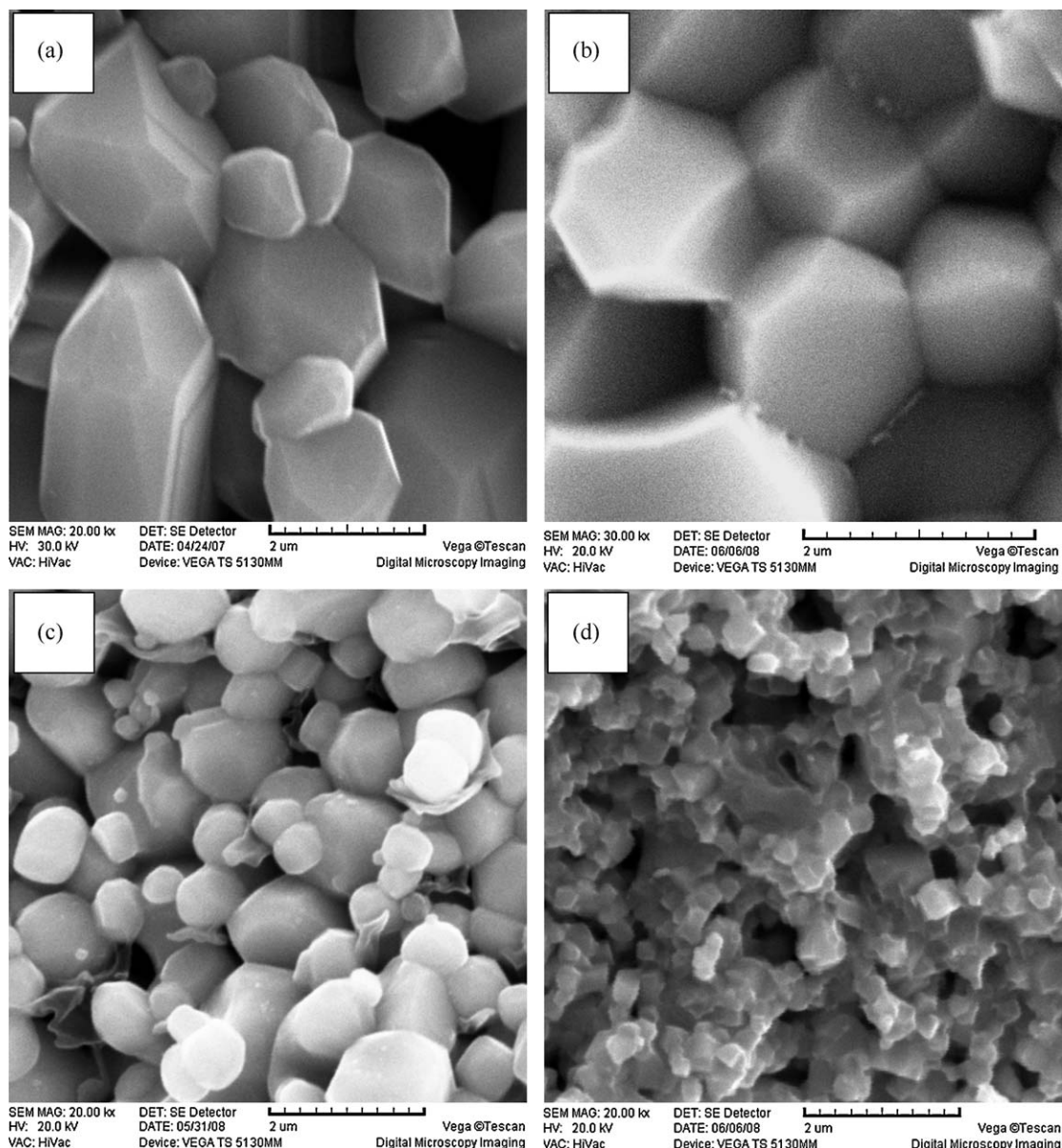
Fig. 4. Micrographs of barium titanate specimens sintered at 1300 °C for 8 h BT, (b) BTL1, (c) BTL3 and (d) BTL5.

Table 2
Average grain size and density value for different specimens of barium titanate ceramics.

Sample	Sintering time (h)	D_{SEM} (μm)	Density (g/cm^3)
BT	2	2.0–4.0	85.2
	4	1.5–2.0	88.3
	8	1.0–2.5	90.1
BTL1	2	0.7–0.8	69.5
	4	1.2–1.5	70.2
	8	1.5–1.8	74.6
BTL3	2	0.6–0.8	75.1
	4	0.8–1.0	78.3
	8	0.75–1.0	85.1
BTL5	2	0.3–0.6	81.3
	4	0.3–0.65	83.6
	8	0.2–0.4	87.0

about 0.7 μm with a small amount of grains about 1 μm. For BTL5 samples the average grain size is about 0.5 μm, indicating that higher concentration of lanthanum inhibits grain growth. The grains are rounded or polygonal in shape with large pores. Increasing sintering time the grain growth intensifies. Therefore average grain size ∼1.5 μm is found in BTL1 samples after sintering for 4 h, while BTL3 samples sintered for the same time show average grain size ∼1 μm. BTL5 samples consist of small grains with average grain size of about 0.3 μm, confirming the influence of added La concentration. The microstructure of samples sintered for 8 h and doped with various concentration of lanthanum follows the same trend as previous. The microstructure consists of polygonal grains, where BT doped with the highest lanthanum concentration possess small grains from 0.2 to 0.4 μm. Thus, it

can be noted that lanthanum concentration has significant influence on BT grain growth. As the concentration of lanthanum increases the average grain size decreases.

The dielectric properties of BT, BTL3 and BTL5 ceramics obtained by polymeric precursor method and sintered for 8 h at 1300 °C have been studied. The temperature dependence of dielectric constant was established in the temperature range −175 to 175 °C. Measurements were performed at frequencies of 1, 100 kHz and 1 MHz. The temperature dependence of dielectric constant as a function of donor concentration is presented in Fig. 5.

The dielectric anomalies corresponding to three structural transitions (cubic to tetragonal T_{C-T}, tetragonal to orthorhombic T_{T-O}, orthorhombic to rhombohedral T_{O-R}) can be apparently observed for pure BT sample (Fig. 5a), whereas in doped samples (Fig. 5b,c) lower temperature phase transformations cannot be

clearly detected. The positions of peaks of all structural transitions are shifted to lower temperatures. Peaks become more broaden as the concentration of lanthanum increases. These plots also point out that the addition of lanthanum leads to increase of dielectric constant value. Observed temperature peaks for all structural transformation and dielectric constant value at 1 kHz for all samples are given in Table 3.

Some authors proposed two factors which can be responsible for this behavior. Lowering of T_C with lanthanum concentration may occur due to smaller size of La^{3+} (1.15 Å) as compared to Ba^{2+} (1.35 Å) which makes tetragonal phase unstable or due to creation of titanium vacancies which destroy Ti–O–Ti linkages, responsible for ferroelectricity.

These results point out to the influence of grain size on dielectric constant value as well. As grain size of samples becomes smaller by the influence of lanthanum concentration,
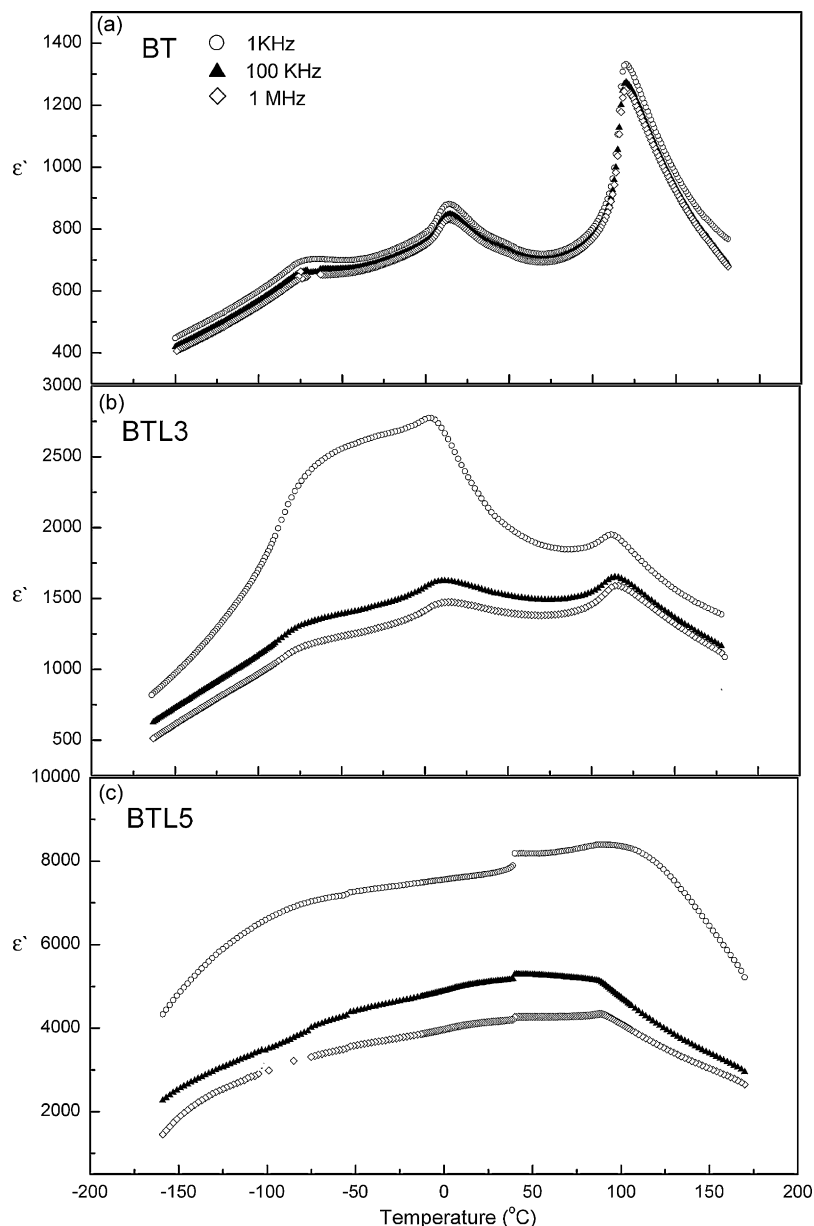

Fig. 5. Temperature dependence of dielectric constant at 1, 100 kHz and 1 MHz for (a) BT, (b) BTL3 and (c) BTL5 samples.

Table 3
Transition temperatures and dielectric constant values for all samples at 1 kHz.

Sample	T_{C-T} (°C)	T_{T-O}(°C)	T_{O-R}(°C)	ε' (T_{room})	ε' (T_C)
BT	120	13	−74	730	1336
BTL3	111	5	−78	2250	1800
BTL5	96	−12	–	7732	8421

dielectric constant becomes higher. In the previous papers this occurrence was also noticed. Otherwise, some authors [17–19] have connected the lowering of T_C with grain size decrease and this is in agreement with results obtained in our study.

Dielectric losses of all samples follow the same trend, they are decreasing with temperature and increasing as concentration of lanthanum becomes higher (Fig. 6).

The frequency dependence of dielectric constant and dielectric losses at room temperature is given in Fig. 7. It can be noted that dielectric constant and dissipation factor in the pure BT are independent of frequency. The dielectric constant for doped samples decreases rapidly with frequency increasing and then reaches a constant value. Therefore, the addition of different concentration of lanthanum could be an effective way to control grain size and adjust dielectric behavior.

Regarding the electrical resistivity, samples of pure BT are electrically insulating at room temperature, however plot presented in Fig. 8 shows the characteristic PTCR effect for doped samples, with rise of resistivity at the Curie point. This resistivity change was higher in the case of lower dopant concentration. The room temperature resistivity and resistivity maxima for BTL3 sample were 1.31×10^5 and $4.18 \times 10^5 \, \Omega$ cm, respectively and for BTL5 were 1.92×10^4 and $5.4 \times 10^4 \, \Omega$ cm.

More deep study about PTCR behavior of La-doped barium titanate samples obtained by polymeric precursor method will be subject of the future research.
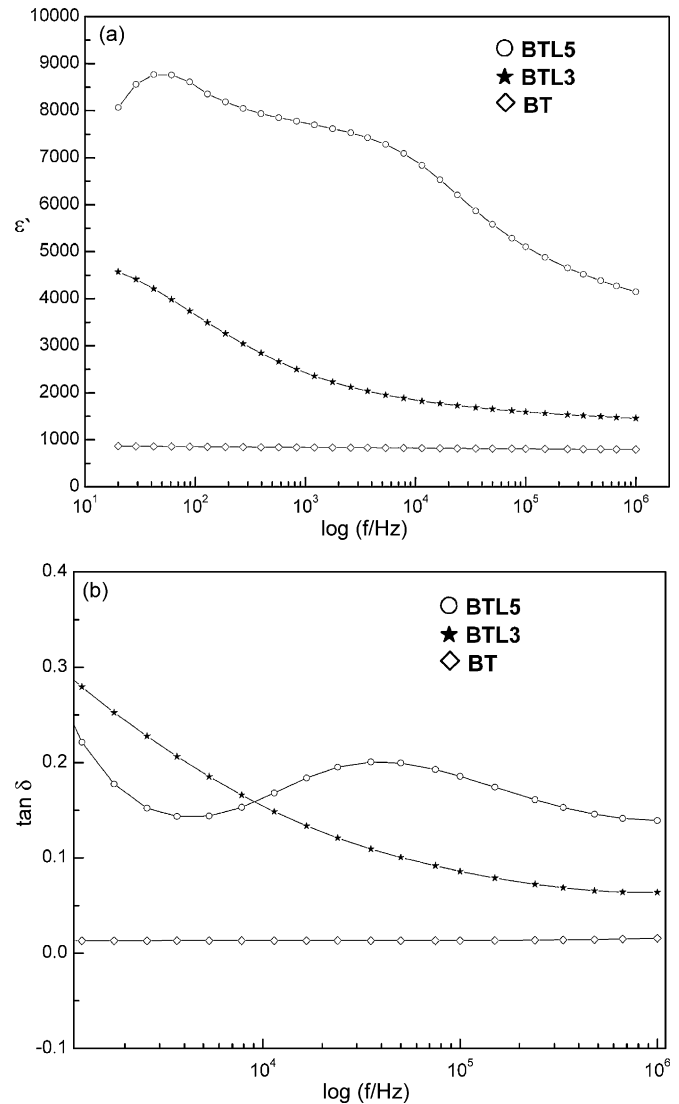

Fig. 7. Frequency dependence of (a) dielectric constant and (b) dissipation factor for pure and La-doped BT samples at room temperature.
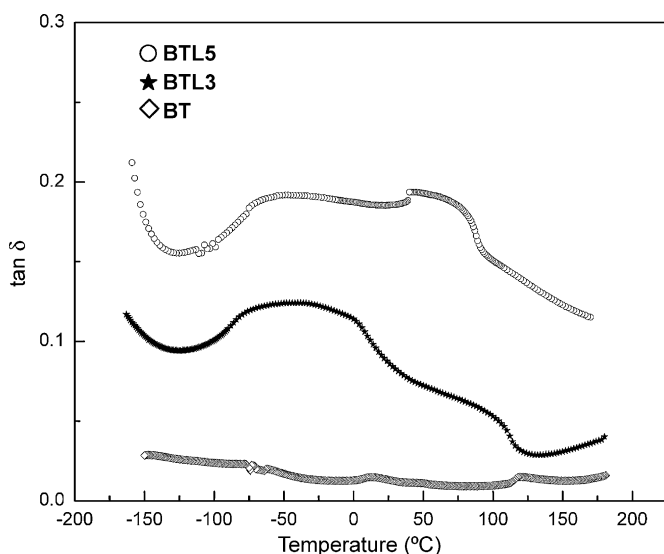

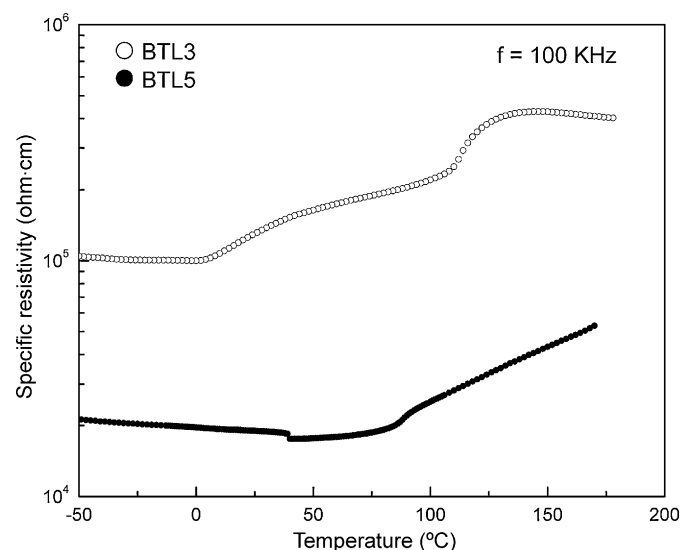Fig. 6. Dissipation factor of all samples measured at 100 kHz.

Fig. 8. Temperature dependence of specific resistivity in PTCR BaTiO₃ at 100 kHz.

4. Conclusion

Nanopowders of BT pure and doped with different concentration of lanthanum were prepared by Pechini process. It was approved that by using this method it could be produced fine cubic BT nanopowder with particles around 20–40 nm. After sintering it was detected well crystallized tetragonal phase in all sintered samples. By changing of sintering time, its influence on increasing of grain size was approved. Lanthanum concentration has effect on grain growth, as the lanthanum concentration increases, the grain size becomes smaller. BT doped with 0.5 mol% of lanthanum sintered for 8 h possesses the highest density. Dielectric measurements of pure and doped BT confirmed that dielectric constant is strongly dependent on the grain size as well as on dopant concentration. Lanthanum concentration influences on shifting of the Curie temperature to the lower temperatures and increase of dielectric constant. It was pointed out that dielectric constant of pure BT is frequency independent in comparison with doped samples where the influence of frequency on dielectric constant and dielectric losses is evident. The appearance of PTCR effect was detected in BT doped samples.

This study provides insight into the Pechini process as an innovative method for preparation of nanosized powders with high purity giving the ability to obtain chemically homogenous powders with low dopant concentration. Therefore, the addition of different concentration of lanthanum could be an effective way to control grain size and adjust dielectric behavior.

Acknowledgments

References

[1] B.D. Stojanovic, Advanced in sintered electronic materials, in: B.D. Stojanovic, V.V. Skorokhod, M.V. Nikolic (Eds.), Proceedings of the Ninth World Round Table Conference on Sintering, Kluwer Academic/ Plenum Publishers, New York, (1999), pp. 367–376.

[2] M.T. Biscaglia, V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, Influence of foreign ions on the crystal structure of BaTiO$_3$, J. Eur. Ceram. Soc. 20 (2000) 1997–2007.

[3] F.D. Morrison, D.C. Sinclair, A.R. West, Doping mechanisms and electrical properties of La-doped BaTiO$_3$ ceramics, Int. J. Inorg. Mater. 3 (2001) 1205–1210.

[4] M. Aparna, T. Bhimasankaram, S.V. Suryanarayana, G. Prasad, G.S. Kumar, Effect of lanthanum doping on electrical and electromechanical properties of Ba$_{1-x}$La$_x$TiO$_3$, Bull. Mater. Sci. 24 (5) (2001) 497–504.

[5] P. Yongding, L. Yunhe, Y. Wenhu, Influence of liquid phase on grain growth of Ba$_{0.998}$Ti$_{0.002}$TiO$_3$ ceramics, J. Rare Earths 25 (2007) 167–170.

[6] F.D. Morrison, D.C. Sinclair, A.R. West, Electrical and structural characteristics of lanthanum-doped barium titanate ceramics, J Appl. Phys. 86 (1999) 6355–6367.

[7] V. Vinothini, P. Singh, M. Balasubramanian, Synthesis of barium titanate nanopowder using polymeric precursor method, Ceram. Int. 32 (2006) 99–103.

[8] B.D. Stojanovic, C.R. Foschini, M.A. Zaghete, M. Cilense, J.A. Varela, Microstructure of doped barium titanate prepared from polymeric precursors, Ceramica y Vidro 41 (2002) 190–193.

[9] M.M. Vijatovic, J.D. Bobic, B.D. Stojanovic, P. Bowen, Characterization of barium titanate prepared by polymeric precursors method, in: P. Bowen, N. Jongen (Eds.), Proceedings of the NanoMetro Workshop COST 539, Atelier de Reprographie de l'EPFL, Lausanne, Switzerland, (2008), pp. 33–34.

[10] Z. Xinle, M. Zhimei, X. Zoujiang, C. Guang, Preparation and characterization on nano-sized barium titanate powder doped with lanthanum by sol–gel process, J. Rare Earths 24 (2006) 82–85.

[11] M.M. Vijatović, M.R. Vasić, J.D. Bobić, Lj.M. Živković, B.D. Stojanović, Effect of powder synthesis method on BaTiO$_3$ ceramics, Process. Appl. Ceram. 2 (2008) 27–31.

[12] M.E.V. Costa, P.Q. Mantas, Dielectric properties of porous Ba$_{0.997}$La$_{0.003}$Ti$_{1.0045}$O$_3$ ceramics, J. Eur. Ceram. Soc. 19 (1999) 1077–1080.

[13] A.F. Shimanskij, M. Drofenik, D. Kolar, Subsolidus grain growth in donor doped barium titanate, J. Mater. Sci. 29 (1994) 6301–6305.

[14] W. Luan, L. Gao, J. Guo, Size effect on dielectric properties of fine-grained BaTiO$_3$ ceramics, Ceram. Int. 25 (1999) 727–729.

[15] B.D. Stojanovic, M.A. Zaghete, C.R. Foschini, F.O.S. Vieira, J.A. Varela, Structure and properties of donor doped barium titanate prepared by citrate process, Ferroelectrics 270 (2002) 15–20.

[16] H.T. Kim, Y.H. Han, Sintering of nanocrystalline BaTiO$_3$, Ceram. Int. 30 (2004) 1719–1723.

[17] M. Kuwabara, H. Matsuda, N. Kurata, E. Matsuyama, Shift of the curie point of barium titanate ceramics with sintering temperature, J. Am. Ceram. Soc. 80 (1997) 2590–2596.

[18] A. Bologna Alles, R. Vanalstine, W. Schulze, Dielectric properties and aging of fast-fired barium titanate, Latin Am. Appl. Res. 35 (2005) 29–35.

[19] L. Wu, M.C. Chure, K.K. Wu, W.C. Chang, M.J. Yang, W.K. Liu, M.J. Wu, Dielectric properties of barium titanate ceramics with different materials powder size, Ceram. Int. 35 (2009) 957–960.