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Effect of lanthanum substitution on microstructure and electrical properties of $(Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTi_{0.41}Zr_{0.59}O_3$ ceramics

Panupong Jaiban [a], Sukanda Jiansirisomboon [a,b], Anucha Watcharapasorn [a,b,*]

[a] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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Abstract

Bismuth sodium zirconate (BNZ) based ceramics with a composition of $(Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTi_{0.41}Zr_{0.59}O_3$ where $x = 0$, 0.005, 0.01, 0.02 and 0.03 were prepared by a solid-state mixed oxide method and sintered at the temperature of 900 °C for 2 h. All the samples had relative density between 91 and 97% of their theoretical values. Phase analysis using X-ray diffraction indicated single rhombohedral or pseudo-cubic perovskite structure. SEM showed that addition of La caused the average grain size of the BNTZ ceramics to decrease as well as an improvement of sample density. Dielectric properties at room temperature measured at 10 kHz indicated that addition of La increased the dielectric constant. The results of ferroelectric characterization also revealed that adding La caused a decrease in coercive field without affecting the remanent polarization.
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1. Introduction

Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), a lead-free perovskite-structured ceramic was originally discovered by Smolenskii et al. [1]. In the past few years, several investigations have been made in order to study the electrical properties of solid solutions of $Bi_{0.5}Na_{0.5}TiO_3$ with other perovskite compounds such as $BaTiO_3$ [2,3], $(K_{0.5}Bi_{0.5})TiO_3$ [4,5]. All these attempts have focused on modifying A – site i.e. divalent pseudo-cation $(Na, Bi)^{2+}$. Besides, it has been observed that modification at B-site also played an important role in tailoring various properties of perovskite materials [6,7].

Watcharapasorn et al. [8] attempted to study microstructure and mechanical properties of $Bi_{0.5}Na_{0.5}(Ti_{1-x}Zr_x)O_3$ with $x = 0$, 0.05, 0.1, 0.15 and 0.20. It was found that the density, grain size and hardness increased with increasing Zr content. Furthermore, many researches investigated the phase relationship in $Bi_{0.5}Na_{0.5}(Ti\text{-}B)O_3$ binary systems where B = Zr, $Fe_{0.5}Nb_{0.5}$, $Zn_{0.3}Nb_{0.7}$ or $Mg_{0.3}Nb_{0.7}$ [9]. An interesting result from these studies was the phase diagram of $(Bi_{0.5}Na_{0.5})TiO_3$–$(Bi_{0.5}Na_{0.5})ZrO_3$ which showed the morphotropic phase boundary (MPB) at room temperature for the composition with Zr/Ti ratio ≈ 0.59/0.41. After an extensive literature survey, it was found that no attempt has so far been made to study electrical properties of the compound having this composition. In addition, Herabut and Safari indicated some improvements in dielectric and piezoelectric properties of La-substituted BNT ceramics [10]. Based on these data, this research therefore attempted to study La-doped $Bi_{0.5}Na_{0.5}(Ti_{0.41}Zr_{0.59})O_3$ ceramics in order to exploit the properties of BNTZ ceramic at MPB composition as well as to investigate the effects of lanthanum addition on its microstructure and electrical properties.

2. Experimental

The specimen was fabricated according to the chemical formula $(Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTi_{0.41}Zr_{0.59}O_3$, where $x = 0$, 0.005, 0.01, 0.02 and 0.03. The powders were prepared by a conventional mixed-oxide method. The starting materials used in this study were La_2O_3 (99%, Cerac), ZrO_2 (99%, Riedel-de Haën), TiO_2 (99%, Riedel-de Haën), Bi_2O_3 (98%, Fluka) and Na_2CO_3 (99.5%, RdH). The mixtures of oxides were ball milled

* Corresponding author at: Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: +66 53 94 1921x631; fax: +66 53 94 3445.
E-mail address: anucha@stanfordalumni.org (A. Watcharapasorn).

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in ethanol for 24 h. The mixed powders were dried at 120 °C for 24 h and calcined in a closed alumina crucible at a temperature of 700 °C for 2 h. After sieving, a few drops of 3 wt% PVA (polyvinyl alcohol) binders were added to the mixed powders which were subsequently pressed into pellets with a diameter of 10 mm using a uniaxial press with 1.5-ton weight. Binder removal was carried out by heating the pellets at 500 °C for 1 h. These pellets were then sintered at 900 °C for 2 h dwell time with a heating/cooling rate of 5 °C/min on a covered alumina plate.

Phase identification of powders and ceramics were investigated in 2θ range of 20–90° using an X-ray diffractometer (XRD, Phillip Model X-pert). Bulk densities of sintered ceramics were determined by Archimedes' method. The theoretical densities of all samples were calculated from their X-ray diffraction pattern. Microstructural characterization was performed using a scanning electron microscope (JSM 6335F).

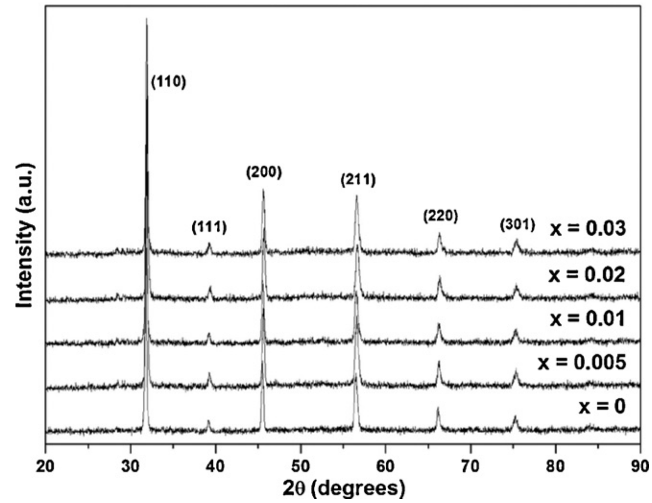

Fig. 1. X-ray diffraction patterns of calcined BNTZ/xLa powders.

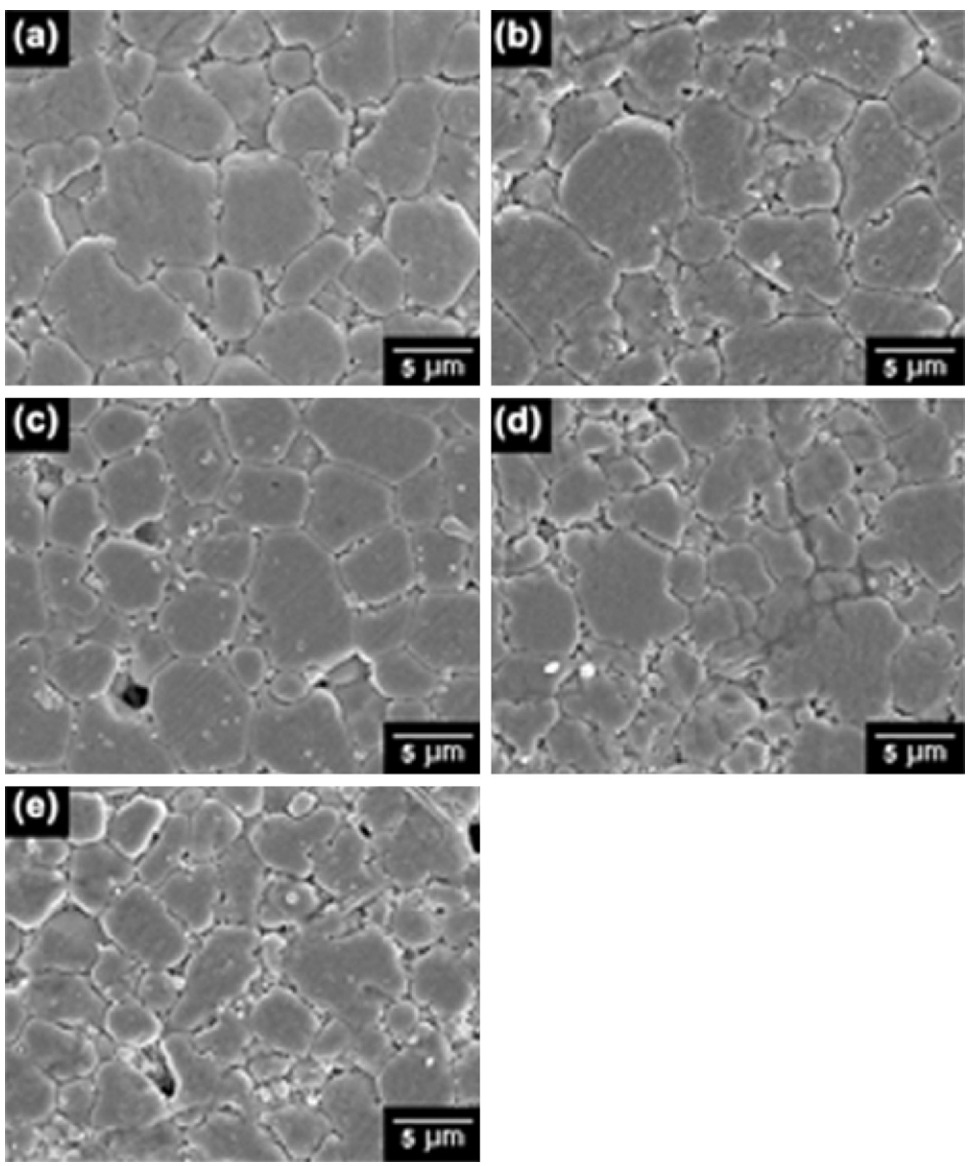

Fig. 2. SEM of BNTZ/xLa ceramics (a) $x = 0$, (b) $x = 0.005$, (c) $x = 0.01$, (d) $x = 0.02$ and (e) $x = 0.03$.

Table 1
Physical, dielectric and ferroelectric properties of BNTZ/xLa ceramics.

La content (at.%)	Relative density (%)	Grain size (μm)	ε_r[a]	tan δ[a]	P_r (μC/cm^2)	E_c (kV/cm)	R_{sq}
0	91	5.91 ± 1.94	238	0.0154	0.11	4.93	0.42
0.005	92	5.79 ± 1.31	243	0.0129	0.11	3.75	0.40
0.01	94	5.68 ± 1.06	254	0.0099	0.10	3.43	0.19
0.02	96	3.93 ± 0.85	274	0.0202	0.07	3.36	0.18
0.03	97	3.85 ± 0.73	285	0.0212	0.10	3.21	0.26

[a] Dielectric data obtained at room temperature and at a frequency of 10 kHz.

For electrical measurements, two parallel surfaces of sintered ceramics were polished and painted with silver paste for electrical contacts. Dielectric properties were measured at room temperature with a measured frequency of 10 kHz using 4284A LCR-meter. Ferroelectric hysteresis loop of each sample was obtained using a computer controlled modified Sawyer–Tower circuit. The electric field was applied to a sample by a high voltage AC amplifier at 30 kV. The polarization–electric field (*P–E*) loop was then recorded by a digital oscilloscope. Remanent polarization (P_r), maximum polarization (P_{max}), coercive field (E_c), maximum field (E_{max}) and loop squareness (R_{sq}) values were then determined from the hysteresis loops.

3. Results and discussion

The XRD patterns of calcined powders of $(Bi_{0.5}Na_{0.5})_{1-x}La_xTi_{0.41}Zr_{0.59}O_3$ with $x = 0$, 0.005, 0.01, 0.02 and 0.03 in a range of $2\theta = 20–90^\circ$ are shown in Fig. 1. It can be seen that, even though $Bi_{0.5}Na_{0.5}(Ti_{0.41}Zr_{0.59})O_3$ was reported to be the MPB composition, the result showed that this material had rhombohedral (or pseudo-cubic) structure. For La-doped BNTZ powders, no observable change in XRD patterns was present. This was due to the small amount of La dopant used as well as the fact that La^{3+} (1.16 Å [11]) had nearly the same ionic radius as those of Bi^{3+} (1.17 Å [11]) and Na^+ (1.18 Å [11]) for the same coordination number (i.e. CN = 8).

Scanning electron micrographs (SEM) of the polished and thermally etched surface of the sintered specimens are given in Fig. 2. It could be seen that, in the case of La^{3+}-free composition (Fig. 2(a)), large grains having average grain size of about 5.9 μm and a few smaller grains were found in this microstructure. Fig. 2(b–e) shows the microstructures of La-doped BNTZ ceramics. It was clearly observed that as the La content increased, the average size of large grains decreased while that of small grains increased. It seemed that La addition helped improve microstructural homogeneity of BNTZ ceramics as shown by the reduced standard deviation listed in Table 1. Furthermore, the densities of La-doped samples were found to be higher than those of un-doped BNTZ ceramics. These results were in agreement with other those of La-doped systems, for examples, $BaTiO_3$ [12,13] and $Bi_4Ti_3O_{12}$ [14,15], in which grain growth inhibition and improvement in densification rate were also observed.

The room temperature dielectric properties of un-doped and La-doped BNTZ ceramics measured at 10 kHz are shown in Fig. 3. $(Bi_{0.5}Na_{0.5})Ti_{0.41}Zr_{0.59}O_3$ ceramic had lowest dielectric constant value of about 238. After addition of La, dielectric constant values were found to increase with increasing La content. These results were partly attributed to an increase in density. Furthermore, based on the composition of BNLTZ ceramics chosen in this study, La^{3+} was expected to replace both Bi^{3+} and Na^+ sites and, hence, to act as donor ions. In this system, therefore, A-site vacancies were expected to be created. Chopra et al. [16] reported that if these vacancies were in the lattice, the transfer of atoms would be easier than that in a perfect lattice and the domain wall motion could be induced by a smaller electric field. Thus, the increase of dielectric constant with increasing La content was also attributed to the increment in the magnitude of dipole moment due to the creation of cation vacancies in BNLTZ ceramics. The dielectric loss values for BNLTZ ceramics roughly showed an increasing trend with increasing La concentration following that of dielectric constant which was another indication of the ease of domain wall motion.

Ferroelectric hysteresis loops of BNTZ and BNLTZ ceramics are shown in Fig. 4. It can be seen that all of the loops were not saturated. Attempts were made to apply higher electric field but it was found that all samples broke down. The remanent polarization (P_r) for all samples was quite low (i.e. ~0.11 μC/cm^2) as compared to that of BNT ($P_r \sim 8.3$ μC/cm^2 [17]). It seemed that BNTZ and BNLTZ ceramics might possess rather high electrical conductivity, causing difficulties in poling and maintaining polarization. In addition, such slim loop characteristics could also be the result of the near-cubic crystal

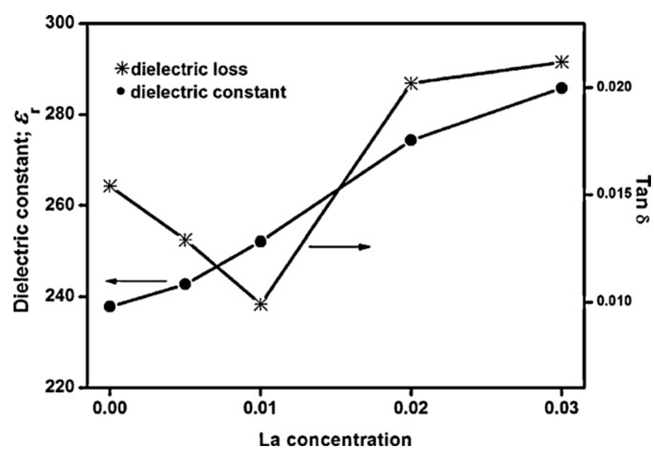

Fig. 3. Plots of dielectric constant and dielectric loss at room temperature at 10 kHz of BNTZ/xLa ceramics with $x = 0$, 0.005, 0.01, 0.02 and 0.03.

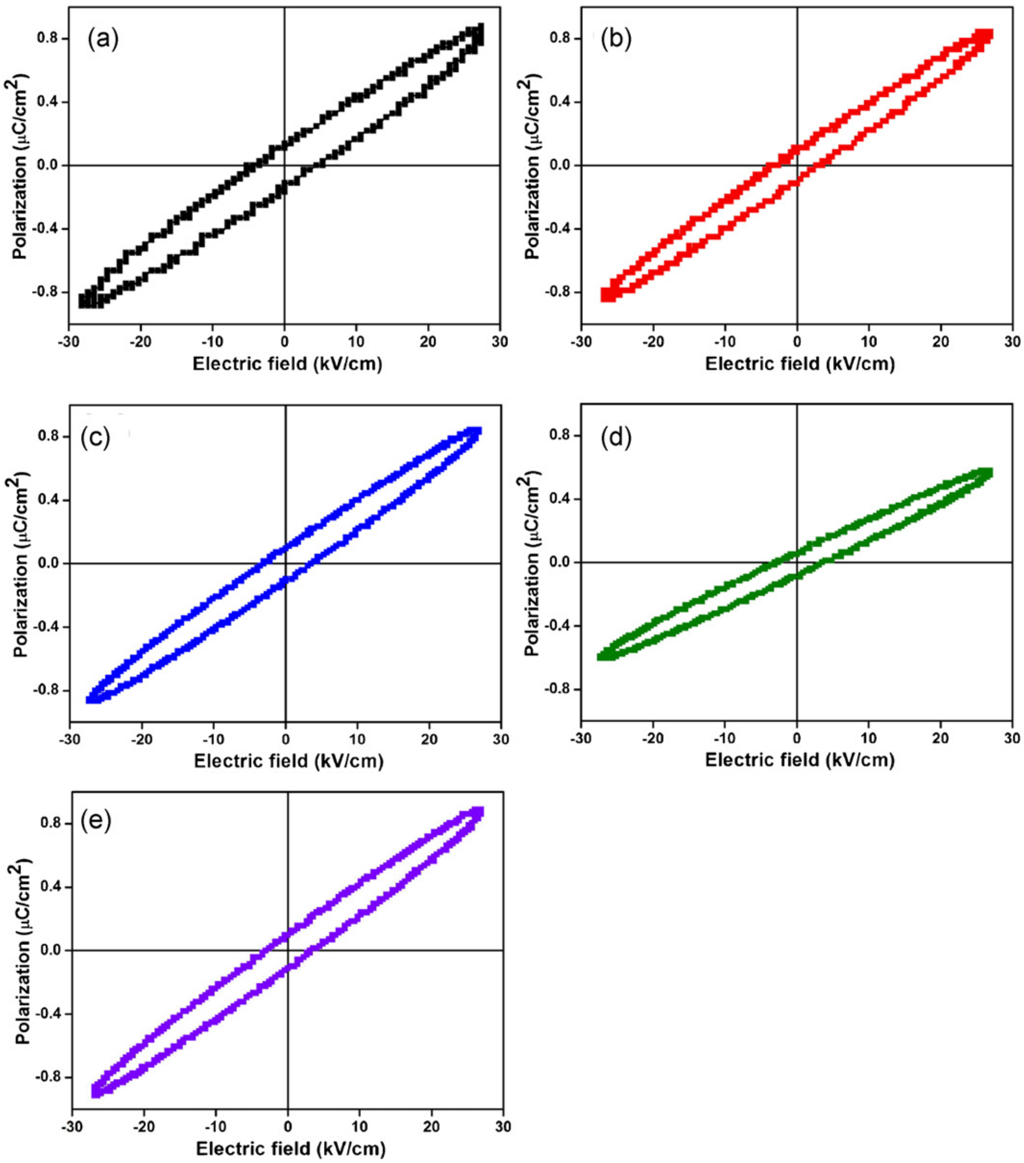

Fig. 4. *P–E* hysteresis loops of BNTZ/*x*La ceramics with $x = 0$, 0.005, 0.01, 0.02 and 0.03.

structure previously mentioned. Nevertheless, in these hysteresis loops, the effect of La addition in BNTZ could be observed from the reduction in coercive field which supported the argument on domain wall movement in this material system.

4. Conclusions

In this study $(Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTi_{0.41}Zr_{0.59}O_3$ ($x = 0$, 0.005, 0.01, 0.02 and 0.03) ceramics were successfully fabricated by a solid-state mixed oxide method. X-ray diffraction patterns indicated that these compounds had a rhombohedral (or pseudo-cubic) structure. A small addition of La caused no change in the crystal structure. However, La apparently inhibited the grain growth and improved microstructural homogeneity as well as density of BNLTZ ceramics. The dielectric constant at room temperature was found to be improved with increasing La content while the dielectric loss remained in the range of 0.01–0.02. For ferroelectric properties, addition of La into BNTZ ceramics had no effect on remanent polarization but caused a decrease in coercive field. From these results, it could be seen that the addition of La could improve dielectric properties of morphotropic phase boundary BNTZ ceramics.

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References

[1] G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, New ferroelectrics of complex composition IV, Soviet Physics Solid State 2 (1961) 2651–2654.

[2] Y. Hosono, K. Harada, Y. Yamashita, Crystal growth and electrical properties of lead-free piezoelectric material $(Na_{1/2}Bi_{1/2})TiO_3$–$BaTiO_3$, Japanese Journal of Applied Physics 40 (2001) 5722.

[3] R. Ranjan, A. Driwedi, Structure and dielectric properties of $((Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3{:}0 \leq x \leq 0.1)$, Solid State Communications 135 (2005) 394.

[4] J. Yoo, D. Oh, Y. Jeong, J. Hong, M. Jung, Dielectric and piezoelectric characteristics of lead-free $Bi_{0.5}(Na_{0.84}K_{0.16})_{0.5}TiO_3$ ceramics substituted with Sr, Materials Letters 58 (2004) 3831–3835.

[5] S. Said, J.P. Mercurio, Relaxor behavior of low lead and lead free ferroelectric ceramics of the $Na_{0.5}Bi_{0.5}TiO_3$–$PbTiO_3$ and $Na_{0.5}Bi_{0.5}$-TiO_3–$K_{0.5}Bi_{0.5}TiO_3$ systems, Journal of the European Ceramic Society 21 (2001) 1333.

[6] T. Wada, K. Toyoike, Y. Imannka, Y. Matsuo, Dielectric and piezoelectric properties of $(A_{0.5}Bi_{0.5})TiO_3$–$ANbO_3$ (A = Na, K) systems, Japanese Journal of Applied Physics 40 (2001) 5703.

[7] H. Ishii, H. Nagata, T. Takenaka, Morphotropic phase boundary and electrical properties of bisumuth sodium titanate–potassium niobate solid-solution ceramics, Japanese Journal of Applied Physics 40 (2001) 5660–5663.

[8] A. Watcharapasorn, S. Jiansirisomboon, T. Tunkasiri, Microstructure and mechanical properties of zirconium-doped bismuth sodium titanate ceramics, Chiang Mai Journal of Science 33 (2006) 169.

[9] Y. Yamada, T. Akutsu, H. Asada, K. Nozawa, S. Hachiga, T. Kurosaki, O. Ikagawa, H. Fujiki, K. Hozumi, T. Kawamura, T. Amakawa, K.I. Hirota, T. Ikeda, Effect of B-ions substitution in $[(K_{1/2}Bi_{1/2})$–$(Na_{1/2}Bi_{1/2})]$ (Ti-B)O_3 system with B = Zr, $Fe_{1/2}Nb_{1/3}$, $Zn_{1/3}Nb_{2/3}$ or $Mg_{1/3}Nb_{2/3}$, Japanese Journal of Applied Physics 34 (1995) 5462–5466.

[10] A. Herabut, A. Safari, Processing and electromechanical properties of $(Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTiO_3$ ceramics, Journal of the American Ceramic Society 80 (11) (1997) 2954–2958.

[11] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallographica A 32 (1976) 751–767.

[12] M. Aparna, T. Bhimasankaram, S.V. Suryanaranana, G. Prasad, G.S. Kumar, Effect of lanthanum doping on electrical and electromechanical properties of $Ba_{1-x}La_xTiO_3$, Bulletin of Materials Science 24 (2001) 497–504.

[13] M.H. Lin, H.Y. Lu, Densification retardation in the sintering of La_2O_3 – doped barium titanate ceramic, Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing 323 (2002) 167–176.

[14] P. Siriprapa, A. Watcharapasorn, S. Jiansirisomboon, Effect of La-doped of phase, microstructure and dielectric properties of $Bi_4Ti_3O_{12}$ ceramics, Advanced Materials 93–94 (2010) 251–254.

[15] P Siriprapa, A. Watcharapasorn, S. Jiansirisomboon, Electrical and mechanical characteristics of $(Bi_{4-x}La_x)Ti_3O_{12}$, Ferroelectrics 382 (2009) 1–6.

[16] S. Chopra, S. Sharma, T.C. Goel, R.G. Mendiratta, Structural dielectric and ferroelectric properties of La doped $PbTiO_3$ sol gel derived thin films, Ferroelectrics 327 (2005) 97–101.

[17] T. Yu, K.W. Kwok, H.L.W. Chan, Preparation and properties of sol–gel-derived $Bi_{0.5}Na_{0.5}TiO_3$ lead-free ferroelectric thin film, Thin Solid Films 515 (7–8) (2007) 3563–3566.