Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 3141–3147

www.elsevier.com/locate/jeurceramsoc

Barium modified lead lanthanum strontium zirconium niobium titanate for dielectric and piezoelectric properties

Koduri Ramam *, Marta Lopez

Departamento de Ingeniería de Materials (DIMAT), Facultad de Ingeniería, Universidad de Concepción, Concepción, Chile

Received 20 September 2006; received in revised form 20 December 2006; accepted 7 January 2007
Available online 6 March 2007

Abstract

The isovalent Ba^{2+} modified lead lanthanum strontium zirconium niobium titanate (PLSZNT) solid solutions were prepared by solid-state reaction method with the compositional formula $[Pb_{1-x-w-y}La_xSr_wBa_y][(Zr_zTi_{1-z})_{(1-(x/4)-(5/4)k)}Nb_k]O_3$ where Ba content, y, was varied from 0, 0.5, 1 and 1.5 mol%. X-ray diffraction (XRD) studies revealed that all the samples have ferroelectric tetragonal structure (FE_{TET}). The presence of multiple ions at Pb-site enhanced grain growth and further addition of Ba concentration resulted in restrained grain growth. Dielectric studies suggested that the ε_{RT} increased up to 1 mol% Ba while T_c has shown a continuous decreasing trend throughout the series. The piezoelectric parameters as a function of grain growth were characterized. The optimum piezoelectric charge coefficient ($d_{33} = 538$ pC/N) and piezoelectric planar coupling coefficient ($k_p = 0.521$) was found to be in 1 mol% Ba modified PLSZNT ceramic, respectively, and this composition may be suitable for possible sensor and actuator applications.

Keywords: Grain size; Dielectric properties; Piezoelectric properties; PLZT; Sensors and actuators

1. Introduction

Ferroelectric ceramics have been widely used in the areas such as dielectric ceramics for capacitor applications, ferroelectric thin films for non-volatile memories, piezoelectric materials for medical ultrasound imaging and actuators and electro-optic materials for data storage and displays, etc.[1,2] PZT has a perovskite type structure (ABO_3) with Pb^{2+} occupying the A-site and the Ti^{4+} and Zr^{4+} ions occupying the B-site at random. $PbZrO_3$ and $PbTiO_3$ modified with La_2O_3 forms lead lanthanum zirconium titanate, also known as PLZT. The incorporation of La^{3+} ions into Pb(Zr,Ti)O_3, ceramics increases their dielectric constants and coupling factors.[3] The influence of various modifiers like Sm,[4] Ba,[5] Sr,[6] Nb,[7] Na,[8] Ag,[9] Dy[10], etc., have been extensively investigated for various specific properties required in either thin films or bulk ceramics. The various modifiers on hard PZT's or soft PZT's both on A-site (Pb) and/or B-site (Zr/Ti) sites with pentavalent, isovalent and/or aliovalent elements or donor/acceptor ions can effect the microstructural development and electromechanical properties of the ceramics. The distribution of A-site and B-site vacancies in PLZT[11] and PT[12] ceramics has been extensively investigated. The ceramic systems of $(Pb_{1-x}X_x)(Zr_{0.7}Ti_{0.3})O_3$ (X = Ca, Sr, Ba) were investigated for dielectric properties in multilayer capacitor (MLC) applications with thin dielectric layers.[6]

In an investigation of the addition of La_2O_3 to $PbTiO_3$, in relation to the partial pressure of PbO,[13] it was found that specimens with only A-site vacancies could be produced at low partial pressures of PbO. All ferroelectric materials having a transition temperature where $T > T_c$ the crystal does not exhibit ferroelectricity, while for $T < T_c$ it is ferroelectric. On decreasing the temperature through the Curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. Particularly, donor elements like La on Pb or Nb on (Zr/Ti) sites have been reported to positively influence the reliability of PZT thin films,[14] although the dielectric and ferroelectric properties seem to be rather decreased in contrast to what should be expected from effects on bulk ceramics.[15] Lead may be substituted by isovalent cations including Ca^{2+}, Ba^{2+}, Sr^{2+} and Cd^{2+}as well as off-valent substitutions such as rare-earth ions Sm^{3+} and Y^{3+} while maintaining the perovskite crystal structure responsible for the strong ferroelectric behaviour.[16] Dausch

---

* Corresponding author. Tel.: +56 41 2203369; fax: +56 41 2203391.
E-mail address: ramamk@udec.cl (K. Ramam).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.01.001

Table 1
Ba modified PLSZNT ceramic compositions

Composition	mol%	Formula
1	$y=0$	$[Pb_{0.9725}La_{0.0125}Sr_{0.015}][(Zr_{0.53}Ti_{0.47})_{0.990625}Nb_{0.005}]O_3$
2	$y=0.5$	$[Pb_{0.9675}La_{0.0125}Sr_{0.015}Ba_{0.005}][(Zr_{0.53}Ti_{0.47})_{0.990625}Nb_{0.005}]O_3$
3	$y=1.0$	$[Pb_{0.9625}La_{0.0125}Sr_{0.015}Ba_{0.010}][(Zr_{0.53}Ti_{0.47})_{0.990625}Nb_{0.005}]O_3$
4	$y=1.5$	$[Pb_{0.9575}La_{0.0125}Sr_{0.015}Ba_{0.015}][(Zr_{0.53}Ti_{0.47})_{0.990625}Nb_{0.005}]O_3$

General formula used for PLBSZNT: $[Pb_{1-x-w-y}La_xSr_wBa_y][(Zr_zTi_{1-z})_{(1-(x/4)-(5/4)k)}Nb_k]O_3$, where $x=\text{La}=1.25$, $w=\text{Sr}=1.50$, $z=\text{Zr}=53$, $k=\text{Nb}=0.5$ and $y=\text{Ba}$ in mol%. Chemical formula used for PLBSZNT: $[Pb_{0.9725-y}La_{0.0125}Sr_{0.015}Ba_y][(Zr_{0.53}Ti_{0.47})_{0.990625}Nb_{0.005}]O_3$.

and Haertling[17] have fabricated PLZT bulk ceramics and thin films (PLZT (2/53/47), PLZT (2/51/49) and PLZT (2/55/45)) with different La concentration modification near MPB region and found higher dielectric constants. Thus, different properties, viz. dielectric, ferroelectric, piezoelectric, etc., can be tailored by substituting Pb with several donor or acceptor cations in the perovskite and also by several synthesis techniques.

The purpose of the present investigation is to partially substitute Pb by Ba, La and Sr near morphotrophic phase boundary (MPB) and Nb at Zr/Ti-site. This paper is aimed at developing a dielectric and piezoelectric system with enhanced dielectric and piezoelectric properties and the effect of isovalent Ba^{2+} (T_c-shifter) on the dielectric and piezoelectric behaviour of PLSZNT ceramics. Accordingly, we have reported the structural, dielectric and piezoelectric properties of PLBSZNT ceramics in which La = 1.25 mol% = 0.0125, Sr = 1.50 mol% = 0.015, Zr = 53% = 0.53, Ti = 47% = 0.47, Nb = 0.5% = 0.005 and Ba is varied from 0, 0.5, 1 and 1.5 mol% = 0, 0.005, 0.010 and 0.015 (refer Table 1). The results obtained from our studies were analyzed and compared to those of the literature.

2. Experimental procedure

2.1. Synthesis of materials

In this study, the PLBSZNT solid solutions were prepared by the solid-state reaction processing technique, starting with analytical reagent grade powders (purity 99.99%) of PbO, La_2O_3, $BaCO_3$, $SrCO_3$, ZrO_2, TiO_2 and Nb_2O_5. The weighed starting reagents were mixed in appropriate stoichoimetric ratios with the addition of excess 5 wt% PbO to compensate lead loss during high temperature sintering to form the final composition with formula: $[Pb_{1-x-w-y}La_xSr_wBa_y][(Zr_zTi_{1-z})_{(1-(x/4)-(5/4)k)}Nb_k]O_3$ abbreviated hereafter as PLBSZNT where $y=0$, 0.5, 1 and 1.5 mol%, respectively. The batch powders were ball milled using zirconia balls and ethanol as media for 24 h. The dried powders were calcined at 950 °C for 4 h in a high purity alumina crucible by maintaining air atmosphere. Calcined powders were ball milled using zirconia balls and ethanol as media for 24 h to crush agglomerates and to minimize the particle size. The calcined fine powders were mixed with 5 wt% polyvinyl alcohol (PVA, as binder) and were compacted into disk shaped samples sizing of 12 mm in diameter and 2–3 mm of thickness using steel die and hydraulic press under uniaxial pressure of 700–900 kg/cm^2. Binder was burned off at 500 °C for 3 h and sintered at 1225–1250 °C for 4 h in a lead-rich environment and fired in closed alumina crucibles to minimize lead oxide volatilization. After sintering process, the samples were cooled to the room temperature along with furnace.

2.2. Structural characterization

The phase formation in the sintered specimens were analyzed by applying X-ray diffraction (XRD) technique (Philips X-ray diffractometer PW-1710) using Cu Kα radiation with Ni filter at room temperature and a step scan from $2\theta = 20°$ to $60°$. As-sintered ceramic surfaces were polished, thermally etched at 1045 °C for 1 h and gold coated using a sputtering technique to analyze microstructure. Microstructural studies were observed through scanning electron microscopy (SEM) of JEOL Model JSM 840A. Fractured surfaces of the ceramics were also coated with gold for SEM studies. The grain sizes were measured by the linear interception method[18] with scanning electron micrographs. The apparent densities of sintered ceramics were measured using the Archimedes method.

2.3. Dielectric and piezoelectric characterization

The lapped pellet surfaces were painted with silver paste and cured at 600 °C for 1 h to form perfect electrodes on the sample surfaces and these specimens were characterized for room temperature dielectric constant (ε_{RT}), dielectric maximum (ε_{Tc}), Curie temperature (T_c) and dissipation factor ($\tan\delta$) at 1 kHz using 4192A HP Impedance Analyzer. In this study, the temperature change was provided by an automatic temperature chamber (Delta 2300) controlled by a HP computer.

The electroded specimens were poled in silicone oil bath at 100 °C by applying a dc field 20 kV/cm. After 24 h ageing, the poled specimens were characterized for the piezoelectric properties. The piezoelectric planar coupling coefficient (k_p) was characterized using a 4192A HP impedance analyzer through resonance and anti-resonance technique. The piezoelectric charge coefficient (d_{33}) was characterized using a Berlincourt piezo-d-meter.

3. Results and discussion

3.1. XRD studies of barium modified PLSZNT ceramics

Fig. 1(i–iv) depict the XRD patterns of PLSZNT and PLBSZNT ceramics. XRD results demonstrate that all the samples

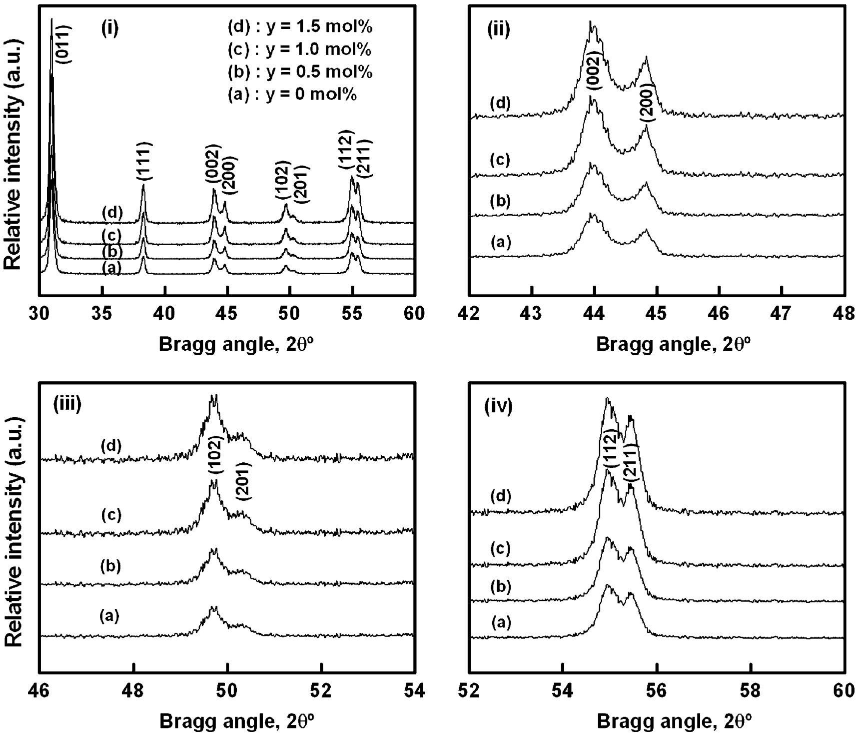

Fig. 1. (i–iv) XRD patterns of PLSZNT and PLBSZNT ceramics.

have a single phase with ferroelectric tetragonal structure and the isovalent Ba^{2+} addition influenced the FE_{TET} phase to intensified ferroelectric tetragonal phase near the MPB where Zr/Ti = 53/47. Fig. 1(i) represents the ferroelectric tetragonality in PLSZNT and PLBSZNT ceramic system and the tetragonal peak's splitting has been illustrated in Fig. 1(ii–iv). In Fig. 1(ii–iv), the tetragonal peak's splitting of (0 0 2) and (2 0 0), (1 0 2) and (2 0 1) and (1 1 2) and (2 1 1) occurred at $2\theta = 43.97°$ and 44.83°, 49.69° and 50.33° and 54.95° and 55.45°, respectively. In our chemical compositions (refer Table 1), we have assumed that trivalent La^{3+} ions partially substitute for Pb^{2+} (at A-site) by creating vacancies at B-site and pentavalent Nb^{5+} ions partially substitute for Zr^{4+} (at B-site) to maintain charge balance in the perovskite. The multiple ions (La^{3+}, Sr^{2+} and Ba^{2+}; Table 2[19]) partially substitute for Pb^{2+} (at A-site) and thereby charge-compensation in the perovskite. The distribution of A-site and B-site vacancies in PLZT has been extensively studied by Hardtl and Hennings.[11] These results are in agreement with previous studies.[19–21]

Table 2
Ionic radius of different ions[19]

Ions	Ionic radii (Å)
Pb^{2+}	1.49
Ba^{2+}	1.61
Sr^{2+}	1.44
La^{3+}	1.36
Zr^{4+}	0.89
Ti^{4+}	0.74
Nb^{5+}	0.74

3.2. Microstructure studies of barium modified PLSZNT ceramics

Fig. 2(i) represents grain size variation of PLSZNT and PLBSZNT ceramics and Fig. 2(iii) represents the scanning electron micrograph of 1 mol% Ba modified PLSZNT fractured ceramic surface. The materials average grain size was determined directly from the SEM micrographs by using the linear interception method.[18] The grain size of a ceramic material is a critical microstructure feature. The grain size in piezoelectric materials depends on the material composition and the sintering process. It is reported that average grain size enhanced with the substitution of Sr in PZT[22] and Nb in PZT[23] accordingly the grain boundary between two enhanced grains will have relatively large grain boundary. In this investigation, Ba modification in PLSZNT ceramic system resulted in grain growth up to 1 mol% Ba, and further Ba addition led to restrained grain growth, where excess Ba content restricts the movement of grains across the grain boundary causing inhibited grain growth. It is known that the domain-wall existence and movement contribute considerably to the dielectric, piezoelectric and elastic properties of the PZT and PLZT ceramics.[24–27] The properties of PZT are known to be affected by microstructure, the nature and amount of modifying elements.[1] The average grain size calculated using scanning electron micrograph revealed that grain growth increased (2.41 μm) up to 1 mol% Ba in PLSZNT ceramic and further addition of isovalent Ba^{2+} resulted in restrained the grain growth. This proves that the nature of modifier and its concentrations affect the microstructure development and electromechanical properties of the ceramics. These results are in accordance with the literature.[1,18,24–27]

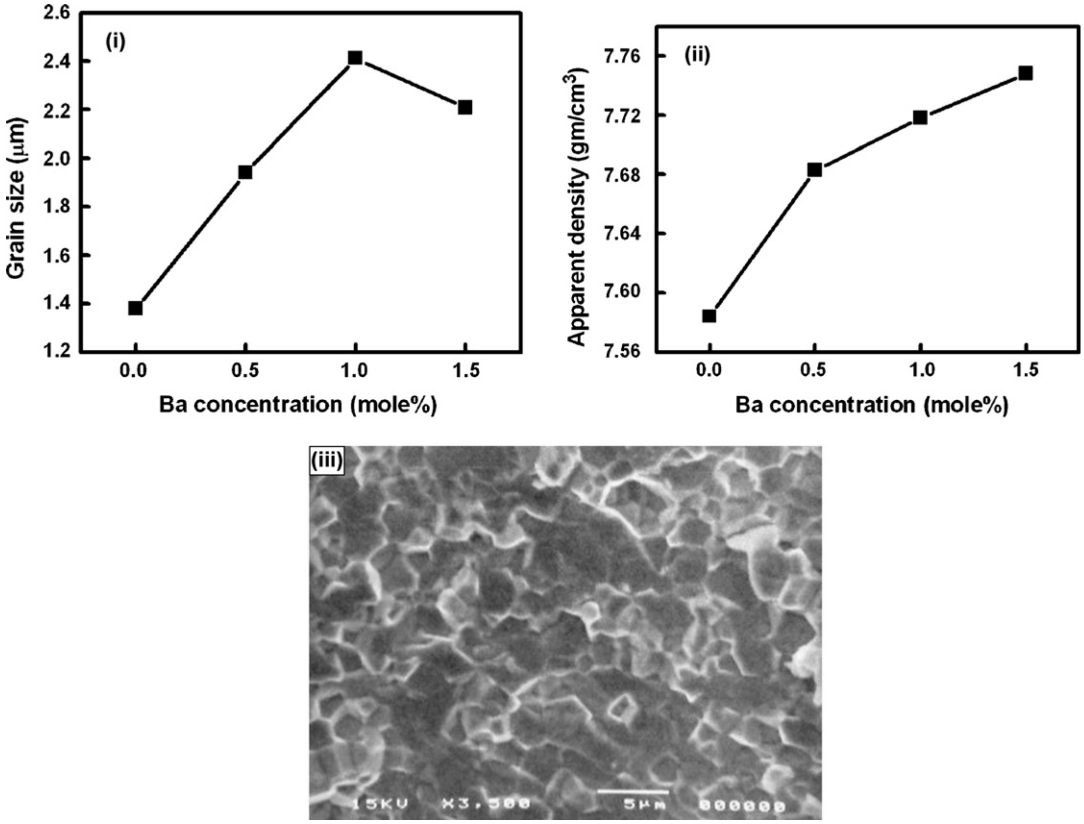

Fig. 2. (i) Grain size variation of PLSZNT and PLBSZNT ceramics. (ii) Apparent density of PLSZNT and PLBSZNT ceramics. (iii) Scanning electron micrograph of 1 mol% Ba modified PLSZNT fractured ceramic surface.

3.3. Apparent density profile of barium modified PLSZNT ceramics

Fig. 2(ii) represents apparent density of PLSZNT and PLBSZNT ceramics. The apparent density is shown as a function of Ba concentration and as the Ba content increased, densification in ceramics achieved up to 1.5 mol% Ba in PLSZNT ceramic system. The barium addition to the PLSZNT at MPB = 53/47 remarkably increased the apparent density of the ceramics in tetragonal phase. At the final stage of sintering, if lead vacancies are formed either by PbO evaporation or by the diffusion of the ions, the densification process is accelerated.

The effect of multiple ions with small additives of isovalent Ba^{2+} has enhanced the diffusion in the perovskite and thereby the outward diffusion of Ba ions speeds up the densification process. The volume diffusion, being the main mechanism, is enhanced by the creation of Pb vacancies and it is controlled by the number of vacancies caused by modifiers, and thus promoting density.[28] The apparent density showed a maximum value of 7.748 g/cm^3 at 1.5 mol% Ba. These results are consistent with the previous investigations.[28–31]

3.4. Dielectric behaviour of barium modified PLSZNT ceramics

Fig. 3(i–iv) shows: (i) room temperature dielectric constant (ε_{RT}), (ii) dielectric maximum (ε_{Tc}), (iii) dielectric loss ($\tan\delta_{RT}$ and $\tan\delta_{Tc}$) and (iv) Curie temperature (T_c) of PLSZNT and PLBSZNT ceramics at 1 kHz, respectively. The enhanced grain growth showed a high dielectric constant at the Curie point. The chemical formulae referred in Table 1 is based on the assumption that Ba^{2+}, Sr^{2+} and La^{3+} partially substitutes for Pb^{2+} in the A-site of the perovskite and that vacancies are created in the B-site to achieve charge balance. The increment of the concentration of lead vacancies allowed the atomic diffusion process during the sintering, thereby achieving better compositional homogenization resulting in dielectric constant increment. As Ba content increased, the room temperature dielectric constant ($\varepsilon_{RT} = 2377$) increased while decreasing dielectric maximum ($\varepsilon_{Tc} = 11182$) at 1 mol% Ba, respectively, with a relatively decreasing room temperature dielectric loss. Usually, the dielectric maximum (ε_{RT}) and dielectric loss ($\tan\delta$) increase simultaneously as an effect of enhanced mobility of domain walls caused by formation of metal vacancies. On contrary, in our study, we observed different tendency, as dielectric maximum increased, the dielectric loss decreased. The Curie temperature showed a continuous decreasing trend from 254 to 229 °C. As can be observed from Fig. 3, Ba^{2+} partially substitutes for Pb^{2+} increasing the dielectric constant while proportionally decreasing the Curie temperature. The multiple donor ions (La^{3+}, Sr^{2+} and Ba^{2+}) partially substitute for Pb^{2+} (at A-site) and pentavalent Nb^{5+} partially substitutes for Zr^{4+} (at B-site), enhancing high dielectric constant with a relatively decreasing Curie temperature and dielectric loss at 1 kHz till 1 mol% Ba. These results comply with previous results.[6,14,17,32–34]

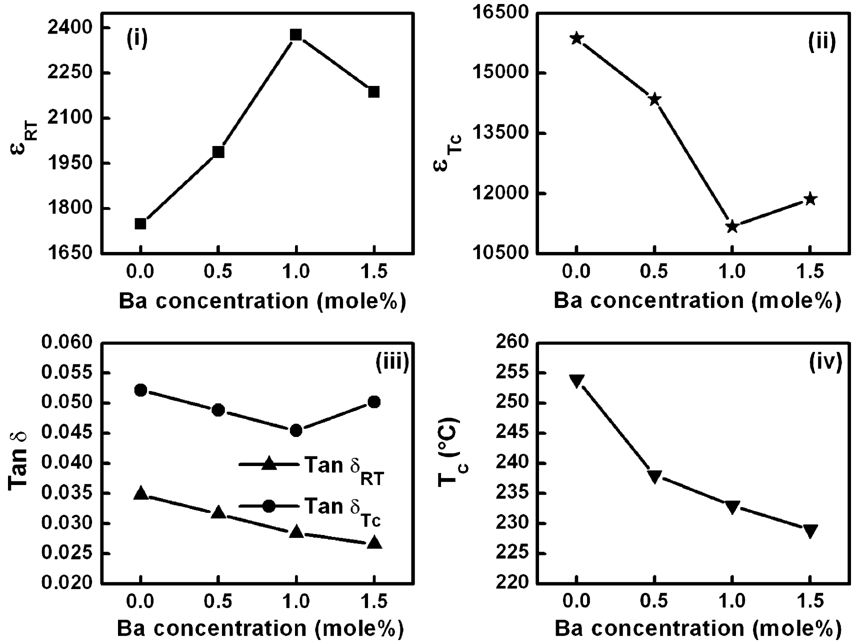

Fig. 3. (i–iv) Room temperature dielectric constant (ε_{RT}), dielectric maximum (ε_{Tc}), (iii) dielectric loss (tan δ_{RT} and tan δ_{Tc}) and (iv) Curie temperature (T_c) of PLSZNT and PLBSZNT ceramics at 1 kHz, respectively.

3.5. Piezoelectric studies of barium modified PLSZNT ceramics

Fig. 4(i and ii) depict piezoelectric charge coefficient (d_{33}) and piezoelectric planar coupling coefficient (k_p) of PLSZNT and PLBSZNT ceramics, respectively. Fig. 5(i and ii) depicts the influence of grain size on piezoelectric charge coefficient d_{33} and piezoelectric planar coupling coefficient k_p of PLSZNT and PLBSZNT ceramics, respectively. It is obvious that the grain size will affect the properties of piezoelectric ceramics. Fig. 5 depicts experimental results of the dependence of piezoelectric properties on average grain size in PLSZNT and PLBSZNT ceramics. In general, piezoelectric properties of ceramics increase approximately linearly with increasing grain size. In PZT ceramics with a tetragonal phase (titanium-rich) and in $PbTiO_3$ ceramics, both 180° and 90° domain walls exist near the MPB. Usually, 180° domains are switched sufficiently by an external field and are stable in a poled sample.[2] There are several parameters influencing the properties of piezoelectric materials, viz. homogeneity, porosity, grain size and different cationic concentrations, etc. However, it is worth noting that the most striking effects of the grain size are on mechanical rather than on electrical properties. Piezoelectric properties are also sensitive to isovalent substitutions (Ba^{2+} and Sr^{2+}) of the cations and formation of end product solid solutions. The piezoelectric charge coefficient ($d_{33} = 538$ pC/N) and piezoelectric planar coupling coefficient ($k_p = 0.521$) had increased up to 1 mol% Ba, respectively. The increasing grain size relatively enhanced the piezoelectric properties till 1 mol% Ba and further increment of isovalent Ba^{2+} additive controlled the d_{33} and k_p in 1.5 mol% Ba. Our results are in conformity with those of Ikeda[27] in which it is clear that with increasing concentration of modifiers after attaining saturation, there is a decrease in the piezoelectric properties. It was revealed that penetration of oxygen into PLZT plays dominant role in controlling electromechanical performance, while increased grain growth influenced piezoelectric properties. These results comply with the literature.[2,22,29,35–37]

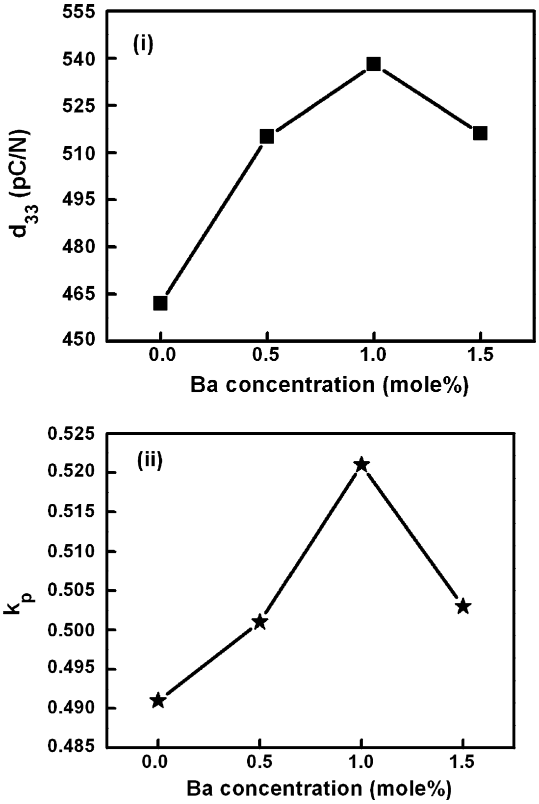

Fig. 4. (i and ii) Piezoelectric charge coefficient (d_{33}) and piezoelectric planar coupling coefficient (k_p) of PLSZNT and PLBSZNT ceramics, respectively.

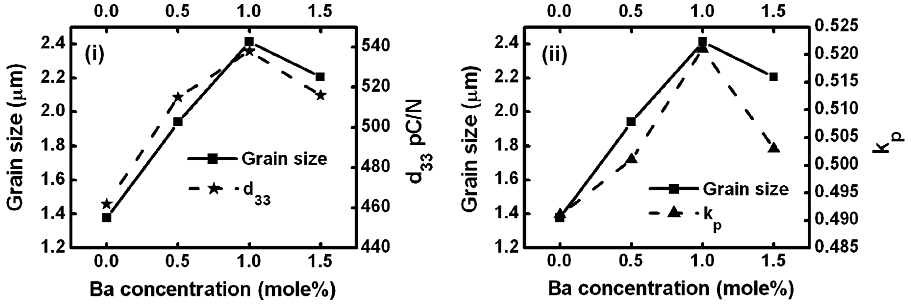

Fig. 5. (i and ii) Influence of grain size on piezoelectric charge coefficient d_{33} and piezoelectric planar coupling coefficient k_p of PLSZNT and PLBSZNT ceramics, respectively.

4. Conclusion

The presence of multiple ions at A-site in the perovskite and average grain growth increment play an important role in the compositional and microstructural homogenization of PLBSZNT ceramic system. The increase of isovalent Ba^{2+} additive enhanced grain growth. Microstructural studies revealed that increased grain growth had influenced the density, dielectric and piezoelectric properties. The multiple donor ions (La^{3+}, Sr^{2+} and Ba^{2+}) partially substitute for Pb^{2+} (at A-site) and pentavalent Nb^{5+} partially substitutes for Zr^{4+} (at B-site), which resulted in enhanced dielectric constant with relatively decreasing Curie temperature. It has been observed that there is a remarkable influence of Ba on microstructure, which in turn influences the piezoelectric properties (k_p and d_{33}) in PLBSZNT ceramic system. The 1 mol% Ba composition showed optimum values of ε_{RT}, k_p, d_{33} and low tan δ among the series which can be suitable for possible sensor and actuator applications.

Acknowledgements

The authors would like to thank University of Concepcion for the financial assistance extended. The authors would also like to thank Ms. C. Neeladevi for the technical assistance and valuable suggestions provided during this work.

References

1. Jaffe, B., William, R. C. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London and New York, 1971, pp. 101–210.
2. Xu, Y., *Ferroelectric Materials and Their Applications*. North Holland, Amsterdam, 1991, pp. 120–145.
3. Carl, K. and Hardtl, K. H., Structural and electromechanical properties of La-doped $Pb(Ti_{1-x}Zr_x)O_3$ ceramics. *Ber. Deut. Keram. Ges.*, 1970, **47**(10), 687–691.
4. Prakash, C. and Thakur, O. P., Effects of samarium modification on the structural and dielectric properties of PLZT ceramics. *Mater. Lett.*, 2003, **57**, 2310–2314.
5. Ramam, K. and Miguel, V., Microstructure, dielectric and ferroelectric characterization of Ba doped PLZT ceramics. *Eur. Phys. J. Appl. Phys.*, 2006, **35**, 43–47.
6. Kanai, H., Furukawa, O., Abe, H. and Yamashita, Y., Dielectric properties of $(Pb_{1-x}X_x)(Zr_{0.7}Ti_{0.3})O_3$ (X = Ca, Sr, Ba) ceramics. *J. Am. Ceram. Soc.*, 1994, **77**, 2620–2624.
7. Aoki, T., Kuwabara, M., Kondo, M., Tsukada, M., Kurihara, K. and Kamehara, N., Micropatterned epitaxial $(Pb,La)(Zr,Ti)O_3$ thin films on Nb-doped $SrTiO_3$ substrates by a chemical solution deposition process with resist molds. *Appl. Phys. Lett.*, 2004, **85**(13), 2580–2582.
8. Shannigrahi, S., Choudhary, R. N. P., Acharya, H. N. and Sinha, T. P., Phase transition in sol–gel derived sodium modified PLZT (8/60/40) ceramics. *J. Phys. D: Appl. Phys.*, 1999, **32**, 1539–1547.
9. Grekhov, I., Delimova, L., Liniichuk, I., Mashovets, D. and Veselovsky, I., Strongly modulated conductance in Ag/PLZT/LSCO ferroelectric field-effect transistor. *Ferroelectrics*, 2003, **286**(1), 237–244.
10. Zhang, Y., Zeng, X., He, X., Ding, A. and Yin, Q., The microstructure and properties of dysprosium ions doped PLZT ceramics. *Integr. Ferroelectr.*, 2006, **78**(1), 215–220.
11. Hardtl, K. H. and Hennings, D., Distribution of A-site and B-site vacancies in $(Pb,La)(Ti,Zr)O_3$ ceramics. *J. Am. Ceram. Soc.*, 1972, **55**(5), 230–231.
12. Hennings, D. and Hardtl, K. H., Distribution of vacancies in lanthanum-doped lead titanate. *Phys. Status Solidi (a)*, 1970, **3**(2), 465–474.
13. Hennings, D., Range of existence of perovskite phases in the system $PbO–TiO_2–La_2O_3$. *Mater. Res. Bull.*, 1971, **6**(5), 329–339.
14. Voisard, C., Brooks, K. G., Reaney, I. M., Sagalowicz, L., Kholkin, A. L., Xanthopoulos, N. *et al.*, Sol–gel processing of PNZST thin films on Ti/Pt and Tac/Pt metallizations. *J. Eur. Ceram. Soc.*, 1997, **17**, 1231–1238.
15. Klissurska, R. D., Brooks, K. G., Reaney, I. M., Pawlaczyk, C., Kosec, M. and Setter, N., Effect of Nb doping on the microstructure of sol–gel-derived PZT thin films. *J. Am. Ceram. Soc.*, 1995, **78**, 1513–1520.
16. Dong, M. and Gerhardt, R. A., Electrical characterization of sol–gel derived $Pb(Zr,Ti)O_3$ ceramics. In *Dielectric Ceramic Materials*, ed. K. M. Nair. *Ceramic Transactions*, *Vol. 100*. American Ceramics Society, Westerville, 1999, pp. 367–376.
17. Dausch, D. E. and Haertling, G. H., Bulk vs. thin film PLZT ferroelectrics. In *Proceedings of the Eighth IEEE International Symposium on Applications of Ferroelectrics*, 1992, pp. 297–300.
18. Mendelson, M. I., Average grain size in polycrystalline ceramics. *J. Am. Ceram. Soc.*, 1969, **52**, 443–446.
19. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, 1976, **A32**, 751–767.
20. Lal, R., Krishnan, R. and Ramakrishnan, P., Transition between tetragonal and rhombohedra1 phases of PZT ceramics prepared from spray dried powders. *Br. Ceram. Trans. J.*, 1988, **87**(3), 99–102.
21. Galassi, C., Roncari, E., Capiani, C., Fabbri, G., Piancastelli, A., Peselli, M. *et al.*, Processing of porous PZT materials for underwater acoustics. *Ferroelectrics*, 2002, **268**, 47–52.
22. Banerjee, A., Bandyopadhyay, A. and Bose, S., Influence of La_2O_3, SrO, and ZnO addition on PZT. *J. Am. Ceram. Soc.*, 2006, **89**, 1594–1600.
23. Pan, M. J., Rayne, R. J. and Bender, B. A., Dielectric properties of niobium and lanthanum doped lead barium zirconate titanate relaxor ferroelectrics. *J. Electroceram.*, 2005, **14**, 139–148.
24. Okazaki, K. and Nagata, K., Effects of grain size and porosity on electrical and optical properties of PLZT ceramics. *J. Am. Ceram. Soc.*, 1973, **56**, 82–86.
25. Celi, L. A., Caballero, A. C., Villegas, M., Frutos, J. D. and Fernandez, J. F., Effect of grain growth control on PZT properties. *Ferroelectrics*, 2002, **270**, 105–110.

26. Zhang, Q. M., Wang, H., Kim, N. and Cross, L. E., Direct evaluation of domain-wall and intrinsic contributions to the dielectric and piezoelectric response and their temperature dependence on lead zirconate–titanate ceramics. *J. Appl. Phys.*, 1994, **75**(1), 454–459.
27. Ikeda, T., Studies on (Ba–Pb)(Ti–Zr)O_3 system. *J. Phys. Soc. Jpn.*, 1959, **14**(2), 168–174.
28. Hammer, M. and Hoffmann, M. J., Sintering model for mixed-oxide-derived lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1998, **81**, 3277–3284.
29. Li, G. and Haertling, G. H., The electrostrictive and related properties of $(Pb_{1-x}Ba_x)_{1-3z/2}Bi_z(Zr_{1-y}Ti_y)O_3$ ceramic system. In *Proceedings of the Eighth IEEE International Symposium on Applications of Ferroelectrics*, 1992, pp. 569–572.
30. Shrout, T. R., Patet, P., Kim, S. and Lee, G. S., Conventionally prepared sub-micrometer lead-based perovskite powders by reactive calcination. *J. Am. Ceram. Soc.*, 1990, **73**, 1862–1867.
31. Haertling, G. H., PLZT electrooptic materials and application—a review. *Ferroelectrics*, 1987, **75**, 25–55.
32. Gridnev, S. A., Pavlova, N. G., Rogova, S. P., Korotkov, L. N. and Zaentsev, V. V., Dielectric properties of strontium and lead based complex perovskites ceramics. In *Proceedings of the Eighth IEEE International Symposium on Applications of Ferroelectrics*, 1992, pp. 630–631.
33. Koduri, R. and Salinas, L. H., Effect of Ba on ferroelectric and piezoelectric properties of the PLZT (1.2/55/45) system. *Phys. Status Solidi (a)*, 2006, **203**, 2119–2127.
34. Gururaja, T. and Subbarao, E. C., Dielectric behavior of PLZT ceramics modified by Ca^{2+}, Sr^{2+}, Nd^{3+} and Y^{3+} ions. *Ferroelectrics*, 1980, **23**, 101–110.
35. Park, S. E. and Shrout, T. R., Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *J. Appl. Phys.*, 1997, **82**, 1804.
36. Nasar, R. S., Cerqueira, M., Longo, E., Varela, J. A. and Beltran, A., Experimental and theoretical study of the ferroelectric and piezoelectric behavior of strontium-doped PZT. *J. Eur. Ceram. Soc.*, 2002, **22**, 209–218.
37. Maher, G. H., Effect of silver doping on the physical and electrical properties of PLZT ceramics. *J. Am. Ceram. Soc.*, 1983, **66**, 408–413.