Effect of Sintering Time on Dielectric and Piezoelectric Properties of Lanthanum Doped Pb(Ni$_{1/3}$Sb$_{2/3}$)-PbZrTiO$_3$ Ferroelectric Ceramics

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ABSTRACT

Lead zirconate titanate (PZT) based materials can be employed for power harvesting applications since they can produce electrical output in response to ambient pressures, vibrations, movements etc. In the present studies, sintering time for composition $Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$ *(La-PNS-PZT)* was optimised to achieve properties suitable for power harvesting. Composition was processed through mixed oxide route and sintered at 1270 °C for 20 min, 40 min, 60 min, 80min and 100 min. XRD pattern indicated the presence of both, ferroelectric tetragonal and ferroelectric rhombohedral perovskite phases. The optical photographs shown the uniform and dense microstructure for the samples sintered for 60 min, resulted into optimum piezoelectric charge coefficient, voltage coefficient, electromechanical coupling coefficient and figure of merit. Power harvesting capabilities in response to impact of stainless steel ball (8.25 gm) from 150 mm height were evaluated and compared with PZT type 5A. *La-PNS-PZT* produced batter electrical output (5.11 W, 71.13 µJ) across the matching load resistance of 4000 Ω and 2.08 W maximum power and 20.79 µJ energy by PZT type 5A disc across the matching load resistance of 1000 Ω.

Keywords: Power harvesting, energy harvesting, PNS-PZT ceramics, sintering time effect, piezoelectric

1. INTRODUCTION

Lead zirconate titanate (PZT) based ceramics attracted the technologists and researchers for sensor and actuator applications because of the excellent piezoelectric properties[1,2]. Mechanical quality factor (Q_m), dielectric loss factor (*tan δ*), dielectric constant (K_3^T), piezoelectric charge coefficient (d_{33}), piezoelectric voltage coefficient (g_{33}) are the important parameters which decide the suitability of the material for particular application. Materials with high Q_m and low tan δ are suitable for ultrasonic and high frequency applications. Materials with higher K_3^T and d$_{33}$ are suitable for actuator applications like vibration and noise control, benders, optical positioning etc.[3,4]. Materials with higher g_{33} are useful for sensor applications[5]. Particularly, materials with higher d_{33}, g_{33} and higher figure of merit ($d_{33} x g_{33}$) are suitable for power harvesting applications since they offers higher power output[6-9].

Incorporating the suitable dopant and optimising the process parameters, desired properties can be obtained. Sintering parameters viz. atmosphere, temperature, time and heating rate have significant effect on microstructure and thus on electromechanical properties of the final product[10,11]. Dense microstructure with optimum grain size formed during sintering results in better dielectric and piezoelectric properties[12].

In our earlier studies,effect of *Zr/Ti* ratio[13] and lanthanum concentration[14] on power harvesting properties of ferroelectric composition $Pb(Ni_{1/3}Sb_{2/3})$-$(ZrTi)O_3$were investigated. In the present study, ferroelectric composition $Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$[14] was investigated for the effect of sintering

time on the microstructure and electromechanical properties viz. Qm, kp, K_3^T d_{33}, g_{33} and figure of merit. Study was also aimed towards analysing the suitability of this composition for power harvesting applications and its comparison with PZT type 5A.

2. EXPERIMENTAL

Lanthanum doped $Pb(Ni_{1/3}Sb_{2/3})$-$(ZrTi)O_3$ ferroelectric composition $Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$ *[La-PNS-PZT]* was synthesised by mixed oxide route using the oxides of elements.Raw material powders *NiO* (97%, Acros), Sb_2O_5(99%,LobaChemie),*PbO*(99.5%,WaldiesLtd.,Kolkata), ZrO_2 (99.37%, Loba Chemie) and TiO_2 (98.5%, Travancore Titanium Products) were wet milled in pure water medium for 24 hours. Calcination was performed at 1060 °C followed by wet milling. Phase formation of the calcined powder was analysed from slow scanned X-ray diffraction pattern recorded from 42° to 58° by X-Ray diffractometer (Make -PANalytical, Model-X'pert pro). Powder was granuled using polyvinyl alcohol as a binder. Discs of diameter 29 mm and 1.7 mm thickness were compacted using double ended die punch machine (Make-GMT) by maintaining green density near to 4.8 g/cc. Samples were sintered in lead rich environment at 1270 °C for 20 min, 40 min, 60 min, 80 min and 100 min. They were lapped to 1.2 mm thickness and electroded with silver paste, followed by poling. Microstructure of polished and chemically etched samples was studied using optical microscope.

Capacitance (C at 1 kHz), resonance frequency (f_r), anti

resonance frequency (f_a), Impedance (Z_m) were measured at by Hioki Hi-tester (model 3532). Piezoelectric charge coefficient (d_{33}) was measured by Berlincourt d_{33} meter (CPDT-3330). Dielectric constant (K_3^T), voltage coefficient (g_{33}) coupling factor (k_p) and mechanical quality factor (Q_m) were calculated using standard mathematical relations[15,16].

Electrical output, across the load resistance ranging 15 Ω to 6000 Ω, in response to impact of stainless steel ball (8.25 gm) released from 150 mm height was measured. Voltage output was recorded by oscilloscope Make-Rigol, model-DS1064B. Full width at half maximum (FWHM) was evaluated for positive pulse. Maximum power and energy output by positive pulse was calculated respectively, using Eqns. (1) and (2).

$$P_{max} = V_{max}^2 / R \tag{1}$$

$$E_{max} = P_{max} \times FWHM \tag{2}$$

3. RESULTS AND DISCUSSIONS

Composition shows perovskite phase formation reported in our earlier work[14]. Slow scanned X-ray diffraction pattern of calcined powder (Fig.1) shows presence of ferroelectric tetragonal (F_T) and ferroelectric rhombohedral (F_R) perovskite phases indicated by the splitting in the peak intensity at (200) plane in the triplets viz' (002)T, (200)R and (200)T which was also confirmed by splitting in the peak intensity at (201) and (211) planes[13,14,17-21].

Figures 2(a)-2(e) represent the effect of sintering time on
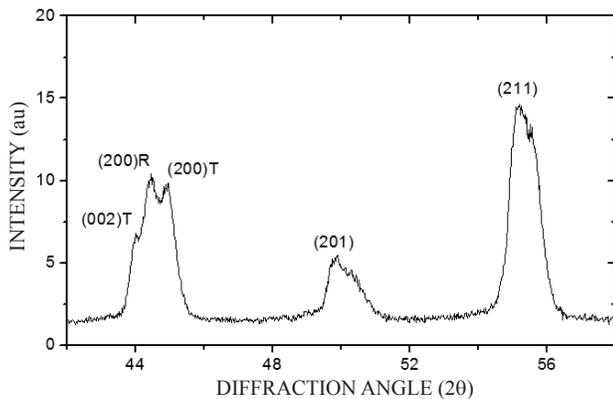

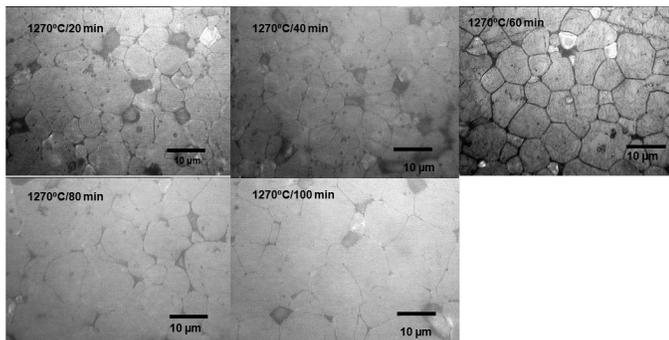**Figure 1. X-ray diffraction pattern of calcined powder.**

Figure 2. Microstructure of samples sintered at 1270 °C for (a) 20 min, (b) 40 min, (c) 60 min, (d) 80 min, and (e) 100 min.

microstructure of the samples sintered at 1270 ºC for 20 min, 40 min, 60 min, 80 min and 100 min, respectively. It was observed that grain size increased with the sintering time. Few grains were polygonal in shape and many ovals in case of the samples sintered for 20 min (Fig 2(a)). Large numbers of pores were also seen. For 40 min sintering time grain size remained same but porosity was reduced. For 60 min sintering time, the grain morphology was remarkably changed. Most of the grains were polygonal, indicating the complete grain growth, which was responsible for the compact microstructure. Narrow grain size distribution with reduced porosity was also noticed. For 80 min and 100 min sintering, grain morphology again changed. Some of the grains were spherical in shape. Broader grain size distribution was observed. Porosity largely increased at triple grain point may be due to the lead loss from the material sintered due to larger sintering time[19]. Loss of compactness in the microstructure was noticed. The average grain size was largely increased.

The average grain size measured by linear intercept method was about 5.99 μm, 6.04 μm, 6.85 μm, 8.76 μm and 10.19 μm of the samples sintered for 20 min,40 min, 60 min,80 min and 100 min , respectively.

Figure 3 shows the effect sintering time on electro-mechanical coupling factor (k_p) and mechanical quality factor (Q_m). As sintering time increased from 20 min to 60 min, k_p increased and reached optimum value (=0.65). This was due increased domain wall motion which promotes the alignment of ferroelectric dipoles along the DC electric field applied during poling[13,14,20]. Increased domain wall motion reduces Q_m and increases k_p[22]. Minimum Q_m was obtained for 60 min sintering time (=128). Further, increasing the sintering time to 100 min, k_p decreased attributing to increased porosity may be due to volatility of *PbO* for larger sintering time (Figs. 2(c)-2(d))[19]. Loss of lead changes the stoichiometry and creates the vacancies at the *Pb* site and reduces the domain wall movement resulting in increase in Q_m and reduction in k_p[23,24].

Figure 4 shows the effect of sintering time on piezoelectric charge coefficient (d_{33}) and on dielectric constant (K_3^T). With increased sintering time from 20 min to 60 min, d_{33} increased
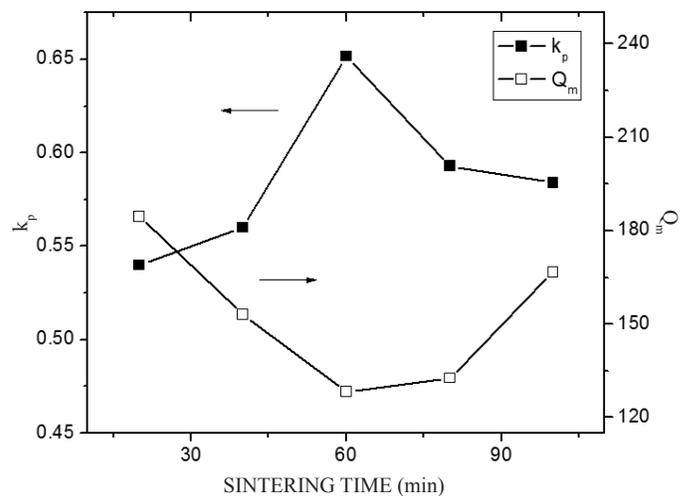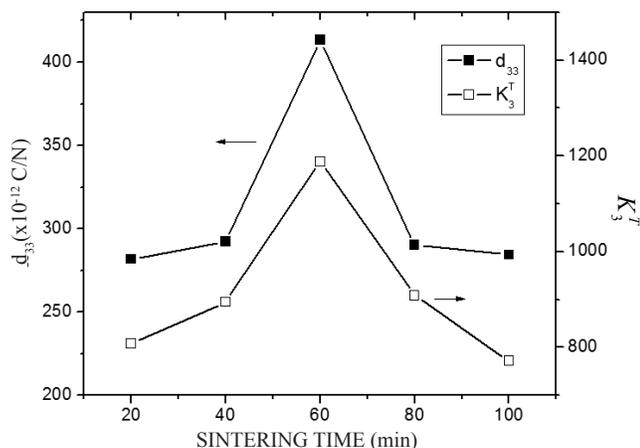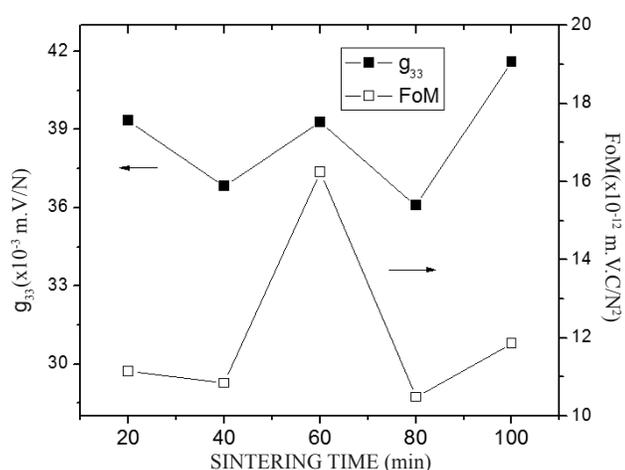

Figure 3. Effect of sintering time on k_p and Q_m.

Figure 4. Effect of sintering time on d_{33} and K^T_3.

Figure 5. Effect of sintering time on g_{33} and FoM.

Figure 6. Electrical output at various load resistances.

Table 1. Electrical out put by La-PNS-PZT and PZT type 5A

Grade parameter	La-PNS-PZT at 4000 Ω	PZT type5A at 1000 Ω
V_{max} (V)	143	45.6
FWHM (μS)	13.91	10
P_{max} (W)	5.11	2.08
Energy (μJ)	71.13	20.79

from 281 x 10^{-12} C/N to 413 x 10^{-12} C/N, which was its optimum value. This was due to the reduced porosity and maximum polarisability obtained at this sintering time. Compactness in the microstructure increases the polarisation per unit volume[13,14,19] resulting into optimum d_{33}. Dielectric constant, K^T_3 increased from 808 to 1188 on increasing the sintering time from 20 to 60 min , which was its optimum value. Further, it decreased to 772 at 100 min sintering time. Dense microstructure with optimum grain size and narrow size distribution obtained for the samples sintered for 60 min was resulted into optimum piezoelectric and dielectric properties of the material[11,23]. On further increasing the sintering time, they were reduced may be due defects in a piezoelectric ceramic structure arose may be due to lead loss and thus increased porosity[16].

Figure 5 shows the effect of sintering temperature on piezoelectric voltage coefficient (g_{33}), and figure of merit (d_{33} xg_{33}), a power generation ability of the piezoceramic. Voltage coefficient (g_{33}) did not show linear relationship with the sintering time. It can be justified from the rise and fall in d_{33} and K^T_3 shown at Fig. 4 and the fact that mathematically, it is directly proportional to d_{33} and inversely proportional to K^T_3. As sintering time increased from 20 mins to 40 mins, extent of increase in d_{33} was less compared to K^T_3 leading to reduction
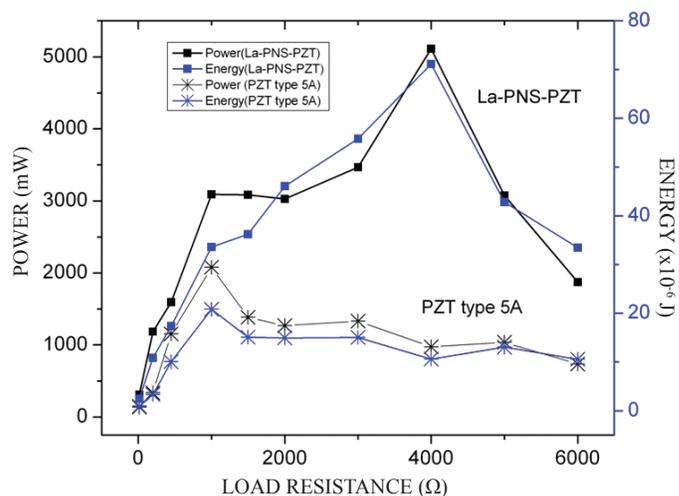
in g_{33}. When sintering time increased from 80 min to 100 min, fall in d_{33} is lesser compared to fall in K^T_3 which yield higher g_{33}. Similarly, trend was shown by *FoM* can be explained on the basis of behavior of d_{33} and g_{33}. Optimum d_{33} and moderate value of g_{33} obtained in the samples sintered for 60 mins., resulted in optimum *FoM*.

In general, impedance is the measure of the opposition to the flow of current through a circuit when an alternating voltage is applied. When impedance of the piezo-element and the load is matched maximum power and thus energy can be obtained[25-27]. It was observed that the power and energy out put given by *La-PNS-PZT* was better than that of PZT type 5A (Fig. 6). The optimum values obtained are given at Table 1. As shown in Fig. 6, maximum power output of 5.11 W and energy output of 71.13 μJ was given by *La-PNS-PZT* across the matching load resistance of 4000 Ω and 2.08 W maximum power and 20.79 μJ energy output is given by PZT type 5A across matching1000 Ω load resistance.

4. CONCLUSIONS

$Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$ ferroelectric composition was synthesised and sintered between 20 mins - 100 mins. XRD pattern indicated the polycrystalline microstructure along with presence of both, ferroelectric tetragonal and ferroelectric rhombohedral perovskite phases. Increased grain size was noticed with the sintering time as seen in optical photographs. Compact and uniform microstructure

with optimum grain size (~$6.85\mu m$) was obtained for the samples sintered for 60 min which was resulted into optimum value of piezoelectric charge coefficient (d_{33}=413 x 10^{-12} C/N), piezoelectric voltage coefficient (g_{33}=39.3 x 10^{-3} V.m/N), electromechanical coupling coefficient k$_p$(0.65), and figure of merit, *FoM* (d_{33} x g_{33}=16.2 x 10^{-12} C.V.m/N^2). It was observed that *La-PNS-PZT* generated higher electrical output compared to PZT type 5A. Optimum power 5.11 W and energy 71.13 *μJ* was generated by *La-PNS- PZT* while 2.08 W power and 20.79 *μJ* energy was generated by PZT type 5A. Comparatively, larger electrical output by *La-PNS-PZT* was attributed to better d_{33}, g_{33} and figure of merit.

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REFERENCES

1. Haertling, G.H. Ferroelectric ceramics: History and technology. *J. Am. Ceram. Soc.*, 1999, **82**(4), 797–818.

2. Jaffe, B.; Cook, W.R. Jr. & Jaffe, H. Piezoelectric ceramic. Academic Press, New York, 1971, pp. 135-43.

3. Jordan, T.L. & Ounaies, Z. Piezoelectric ceramics characterisation. ICASE Report No. 2001-28, NASA/CR-2001-211225. 2001.

4. Zhou, D.; Kamlah, M. & Munz, D. Effects of uniaxial prestress on the ferroelectric hysteretic response of soft PZT. *J. Eur. Ceram*., 2005**, 25**(4), 425-32.

5. Tressler, J.F.; Alkoy S. & Newnham, R. Piezoelectric sensors and sensor materials. *J. Electroceram.*, 1998, **2**(4), 257-71.

6. Kim, H.W.; Priya, S.; Unchino, K. & Newnham, R. Piezoelectric energy harvesting under high pre-stressed cyclic vibrations. *J. Electroceram.*, 2005, **15**(1), 27-34.

7. Mohammadi, F.; Khan, A. & Cass, R.B. Power generation from piezoelectric lead zirconate titanate fiber composites. *In* the Proceedings of the Material Research Society Symposium, Materials Research Society, 2003, 736, pp. D5.5.1-D5.5.6.

8. Green, C.; Mossi, K.M. & Bryant R.G. Scavenging energy from piezoelectric materials for wireless sensor applications. *In* the Proceedings of the ASME International Mechanical Engineering Congress and Exposition, Orlando, USA, November 2005, pp.1-7.

9. Moulson, A.J. & Herbert, J.M. Electroceramics (2nd edition). John Wiley & Sons Ltd., England, 2003, pp. 384.

10. Saha, S.K. & Agarwal, D.C. Composition fluctuations and their influence on the properties of lead zirconate titanate ceramics. *Am.Ceram. Soc. Bull.*, 1992, **71**(9), 1424-29.

11. Kungl, H. & Hoffmann M.J. Effects of sintering temperature on microstructure and high field strain of niobium-strontium doped morphotropic lead zirconate titanate. *J. Appl. Phys.*, 2010 **107**(5), 054111 - 054111-11.

12. Zipparo, M.J.; Shung K.K. & Shrout, T.R. Properties of fine grain PZT materials. *In* the Proceedings of IEEE Ultrasonics Symposium, 1995, **1**, pp. 601 - 604.

13. Lonkar, C.M.; Kharat, D.K.; Kumar, H.H. & Prasad S. Effect of *Zr/Ti* ratio on piezoelectric properties of $Pb(Ni_{1/3}Sb_{2/3})O_3$–$Pb(ZrTi)O_3$ ceramics. *Ceram. Int.,* 2011, **37**(8) 3509-14.

14. Lonkar, C.M.; Kharat, D.K.; Kumar, H.H.; Prasad S. & Balasubramanian, K. Effect of *La* on piezoelectric properties of $Pb(Ni_{1/3}Sb_{2/3})O_3$–$Pb(ZrTi)O_3$ ferroelectric ceramics. *J. Mater. Sci. Mater. Electron.*, 2013, **24**(1), 411-17.

15. Jordan, T.L. & Ounaies, Z. Piezoelectric ceramics characterisation. NASA Langley Research Centre. NASA Report No NASA/CR-2001-211225, 2001.

16. Bing, C.H.; Cheng, L.H. & Long, W. Promotion of piezoelectric properties of Lead Zirconate Titanate ceramics with (*Zr,Ti*) partially replaced by Nb_2O_5. *Solid-State Electron.*, 2004, **48**(12), 2293-97.

17. Yongjian, Yu.; Jinbiao, Tu & Singh, R.N. Phase Stability and ferroelectric properties of lead strontium zirconate titanate ceramics. *J. Am. Ceram.,*2001, **84**(1),333-40.

18. Singh, V.; Kumar, H.H.; Kharat, D.K; Hait, S. & Kulkarni, M.P. Effect of lanthanum substitution on ferroelectric properties of niobium doped PZT ceramics. *Mater. Lett.*, 2006, **60**(24), 2964-68.

19. Wang, M.C.; Haung, M.S.; Tze-Shoeng & Nan-Chung, Wu. Sintering and piezoelectric properties of $Pb(Ni_{1/3}Sb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ ferroelectric ceramics. *J. Mater. Sci*., 2002, **37**(3), 663-68.

20. Laishram, R.; Thakur, O.P.; Bhattacharya, D.K. & Harsh. Dielectric and piezoelectric properties of *La* Doped lead zinc niobate–lead zirconium titanate ceramics prepared from mechano-chemically activated powders. *Mater. Sci. Eng. B*, 2010, **172**(2),172-76.

21. Boutarfafia, A. Investigations of co-existence region in lead zirconate titanate solid solutions: X-ray diffraction studies. *Ceram. Int.,* 2000, **26**(6), 583-87.

22. Sangawar, S.R.; Praveenkumar, B.; Kumar, H.H. & Kharat. D.K., Effect of *Fe* and *Fe-Ba* substitution on the piezoelectric and dielectric properties of lead zirconate titanate ceramics. *Mater. Sci. Eng. B*, 2011,**176**(3), 242-45.

23. Ming, Chen.; Xi, Yao. & Liangying, Zhang. Grain size dependence of dielectric and field–induced strain properties of chemical prepared *(Pb,La)(Zr,Sn,Ti)O$_3$* antiferroelectric ceramics. *Ceram. Int.*, 2002, **28**(2), 201-207.

24. Zahi, S.; Bouaziz, R. & Abdessalem, N. A dielectric and piezoelectric properties of $PbZrO_3$–$PbTiO_3$–$Pb(Ni_{1/3},Sb_{2/3})O_3$ ferroelectric ceramic system. *Ceram. Int*., 2003, **29**(1), 35–39.

25. Umeda, M.; Nakamura, K. & Ueha, S. Energy storage characteristics of a piezogenerator using impact vibration. *Jpn. J. App. Phys.*, 1997, **36**(1), 3146–51.

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