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, 80 min 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 better 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. Mechanical quality factor ($Q_m$), dielectric loss factor ($\tan \delta$), dielectric constant ($K'_3$), 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 $\tan \delta$ are suitable for ultrasonic and high frequency applications. Materials with higher $K'_3$ and $d_{33}$ are suitable for actuator applications like vibration and noise control, benders, optical positioning etc. Materials with higher $g_{33}$ are useful for sensor applications. Particularly, materials with higher $d_{33}$ and $g_{33}$ and higher figure of merit ($d_{33} \times g_{33}$) are suitable for power harvesting applications since they offers higher power output.

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. Dense microstructure with optimum grain size formed during sintering results in better dielectric and piezoelectric properties.

In our earlier studies, effect of Zr/Ti ratio and lanthanum concentration 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$_3$ was investigated for the effect of sintering time on the microstructure and electromechanical properties viz. $Q_m$, $k_p$, $K'_3$, $d_{33}$, $g_{33}$ 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), Sh$_2$O$_3$ (99%, Loba Chemie), PbO (99.5%, Waldies Ltd., 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 \( (f_r) \), 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 \( \Omega \) to 6000 \( \Omega \), 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).

\[
P_{\text{max}} = \frac{V_{\text{max}}^2}{R} \quad (1)
\]
\[
E_{\text{max}} = P_{\text{max}} \times \text{FWHM} \quad (2)
\]

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 microstructure of the samples sintered at 1270 \( ^\circ C \) 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 \( \mu m \), 6.04 \( \mu m \), 6.85 \( \mu m \), 8.76 \( \mu m \) and 10.19 \( \mu m \) 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...
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 output 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 $\mu$J was given by La-PNS-PZT across the matching load resistance of 4000 $\Omega$ and 2.08 W maximum power and 20.79 $\mu$J energy output is given by PZT type 5A across matching 1000 $\Omega$ load resistance.

### 4. CONCLUSIONS

Pb$_{0.98}$La$_{0.02}$Ni$_{0.05}$Sb$_{0.05}$Ti$_{0.995}$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 µm) 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_{31}(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

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