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RESEARCH PAPER

Harvesting Power Through Random Vibrations of Aerospace Vehicles from Nanostructured La-Pb($Ni_{1/3}Sb_{2/3}$) - $PbZrTiO_3$ Ferroelectric Ceramics

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ABSTRACT

Synthesis by mechanochemical activation route and optimisation for power harvesting properties of nano-structured $Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$ [La-PNS-PZT] ferroelectric ceramic composition has been carried out and reported here for the first time. Progressive perovskite phase formation during mechanical activation from 5 h to 40 h followed by reactive sintering was analysed from X-Ray diffraction analysis. Noticeable formation of perovskite phase after 10 h of milling and further its completion in successive reactive sintering was observed. Particle morphology of the 10 h activated nano-La-PNS-PZT powder analysed by high resolution transmission electron microscope indicated average particle size (d_{50}) of about 24 nm. Microstructural studies of samples reactively sintered at 1220 °C were performed by field emission scanning electron microscopy for powders activated for various durations, indicated the compact microstructure for 10 h activation which resulted in optimum piezoelectric properties viz. piezoelectric charge coefficient (d_{33}= 449x10^{-12} C/N), piezoelectric voltage coefficient (g_{33}= 32x10^{-3} m-V/N), Figure of merit for power harvesting (14.4 x10^{-12} V-m-C/N^2) accompanied by excellent stability of permittivity in the range -50 °C to 100 °C. The output voltage obtained from simulated random vibrations of aerospace vehicles at various power spectrum density values, measures about 3.0 mV output across resistance of 1 kΩ indicating suitability of composition for harvesting the power from aerospace vehicle vibrations .

Keywords: Nano- La-PNS-PZT, mechanical activation, power harvesting, random vibration test, Aerospace vehicle vibrations

1. INTRODUCTION

PZT based piezoceramics are electromechanical energy converters, are suitable for sensors, actuators[1-4] and power harvesting applications[5-8] in civil and defence sectors[9]. PZT compounds crystallize in ABO_3 type perovskite structure in which 'A' is a large divalent Pb^{2+} cation occupies the corner of the unit cell. Zr^{4+} and Ti^{4+} are small tetravalent cations occupy the ferroelectrically affected 'B' position at the displaced centre while O^{2-} is the face cantered anion. Due to minimal potential energy considerations, positive and negative charge sites do not coincide and thus form the dipole[8]. Formation of spontaneous dipole due to separation of positive and negative charge centres and further alteration in this separation due to application of stress is the origin of piezoelectricity in perovskite structured PZT compositions[8]. Compositions with superior piezoelectric charge coefficient (d_{33}) are suitable for actuator applications[10,11] while higher values of piezoelectric voltage coefficients lead to generation of higher voltages and hence find suitability for sensor[12] and power harvesting applications[5-8, 13,14].

PZT compositions can be obtained by wet chemical methods like sol-gel, co-precipitation, hydrothermal etc. and dry methods like solid state route[15-17] or mechanical activation (MA) processes[18] for nano crystalline ceramics. Mechanical activation process employees high energy ball mill (HEBM) in which raw material powders are milled intimately by tungsten carbide balls. Due to combined effect of mechanical energy and temperature in the HEBM[18] particles fuzed together and ruptured continuously[19]. This initiates the chemical reaction among raw material powders along with reduction in particle size to nanometre regime, thereby evading the calcination stage of conventional mixed oxide route[20]. Nanomaterials attracted researchers since it creates a possibility of improving the properties due to variation in crystallite size[1,18]. MA process was employed around 1966 by Benjamin for formation of oxide dispersed metal alloys for structural applications[19,21] Since then, it has been widely used by several researchers for preparation of nano PZT based materials. Practically, possibility of contamination of tungsten carbide increases due to availability of larger surface area due to large reduction in particle size and formation of newer surface area for larger milling times[19]. However, this can be overcome by carrying out MA for reduced durations followed by 'Reactive Sintering' to further complete the solid state reaction.

$Pb(Ni_{1/3}Sb_{2/3})O_3$-$PbZrTiO_3$, abbreviated as PNS-PZT, is a solid solution of complex perovskite of type $Pb(B'_{1/3}B''_{2/3})O_3$-$Pb(B)O_3$, have been studied by some of the researchers around its morphotropic phase boundary (MPB) of PNS-PZ-PT (i.e. 0.12 PNS -0.40 PZ -0.48 PT) for various compositional

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modifications, processing parameters and their effects on dielectric and piezoelectric properties[22-26]. The authors of the present work, have also investigated and reported a novelty of a lanthanum doped PNS-PZT compositions [La-PNS-PZT], at MPB of PZT and reported for various properties suitable for power harvesting[2,7], underwater sensor[9] and actuator applications[7,27] during their earlier studies. All these studies were restricted to the compositional powders in micro-meter regime.

In the present study, authors synthesised *Nano*-La-PNS-PZT composition by columbite precursor method, followed by mechanical activation using High Energy Ball Mill. Mechanical activation induced structural effects were correlated with the piezoelectric properties and their optimisation for power harvesting applications. Another goal was to explore the stability of properties over the temperature and suitability of the compositions for power harvesting through random vibrations of aerospace vehicles.

2. EXPERIMENTAL

Nanostructured composition $Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$ of the present study, was synthesised from oxides of elements in the powder form using PbO (Waldies Ltd., India, 99.65%), ZrO_2 (Indian Rare Earths Ltd, India, 99.70 %), TiO_2 (Travancore Titanium Products, India, 98.50 %), NiO (Acros, India 97 %),Sb_2O_5 (Loba Chemie, India 99 %) and La_2O_3 (Indian Rare Earths Ltd., India, 99.99%) by mechanical activation using high energy ball milling process. Pyrochlore-free single perovskite phase La-PNS-PZT ceramic was obtained by synthesising B site precursor $NiSb_2O_6$ [NS] by solid state route in first stage, followed by mechanical activation of NS with remaining oxides using high energy ball mill (Retch, model-PM 400). The powder was activated for 5 h, 10 h, 20 h, 30 h, and 40 h at 300 rpm. We have used ball to powder weight ratio (BPR) as 13:1. The progressive transition of starting oxide powders into desired composition during mechanical activation were investigated from X-ray diffraction patterns recorded for position 2θ from 20° to 60°, step size 0.02°, scan speed 0.1 s/step using CuKα line (λ=1.54 Å) (D8 Advance, Bruker, Germany). Effects of activation on microstructure were analysed using HRTEM (TECNAI G2, FEI). Further, powder was compacted uniaxially to form pellets of density 4.8 g/cc. The pellets were reactively sintered in lead rich atmosphere in covered alumina crucibles at 1220 °C. Surface morphology of polished and chemically etched sintered samples was analysed using FESEM (Sigma, ZEISS, Germany). Lapped pellets (dia. 10 mm x thick. 1 mm) were electroded by fired on silver and poled by applying DC field of 30 kV/cm at 100 °C for 30 min in silicon oil bath. Dielectric properties were measured at 1 kHz using LCR High Tester (HIOKI-3532, Japan). Piezoelectric charge coefficient (d_{33}) was measured at 100 Hz using piezo d_{33} Meter (PM 300 Piezo Test, UK). Piezoelectric voltage coefficient (g_{33}) and figure of merit for power harvesting (FoM_{ph}) were calculated using standard mathematical relations[5,7,22]. Temperature stability of dielectric constant was evaluated in the temperature range between -50 °C and +340 °C using dielectric analyser (Novatherm Quotro, Novocontrol GmbH).

In this study, authors have assumed the specifications generated by Kumar[28], *et al.* Electrical output voltage of test samples in response to simulated random vibrations of aerospace / launch vehicle have been acquired for various power spectrum density, using vibration shaker (Saraswati Dynamics) controlled through vibration controller VR9500 of Vibration Research Corporation. The time domain data is analysed by Inverse Fourier Transform in frequency domain and correlated to power harvesting and microstructure of reactively sintered samples.

3. RESULTS AND DISCUSSIONS

3.1 Crystallographic Analysis

X-ray diffraction patterns for position 2θ form 20° to 60° for Mechanically Activated powder for 5 h to 40 h denoted respectively, by MA-5 to MA-40 and that of corresponding Reactively Sintered samples denoted respectively by RS-5 to RS-40 are as shown in Fig. 1. Patterns for powders demonstrate the progressive transition of oxides into desired perovskite phase. Subsequently, reactive sintering of the same shows the transformation of powders into pure perovskite phase for entire range of activation time. With increasing the activation time, crystallinity improved indicated by reduction in peak widths. Though 5 h milled powder show existence of perovskite phase, it also shows the existence of mixture of starting powders along with traces of $PbTiO_3$[29,30] and $PbZrO_3$[31]. Increasing the milling time to 10 h, mechanically activated solid state reaction is advanced largely, leading to formation of perovskite phase to greater extent indicated by rise in peak intensity of perovskite planes[7,22] and reduction in peaks for starting components. Further increasing the milling duration to 20 h and 30 h, improvement of solid state reaction for formation of La-PNS-PZT in perovskite phase was noticed. For 40 h milling time,

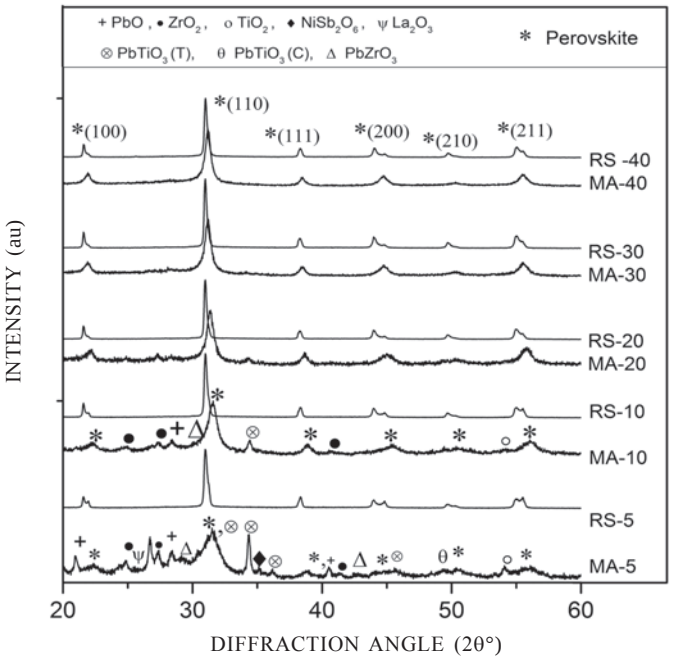

Figure 1. XRD pattern for mechanically activated (MA) Nano-crystalline powder samples and reactively sintered samples (RS).

entire quantity of starting materials are converted into desired La-PNS-PZT composition, which is evident from peaks for single perovskite phase. Though the unreacted starting oxides were present in the activated powders, they get transformed into desired perovskite phase on sintering as indicated by respective XRD patterns (RS-5 to RS-40) along with increase in unit cell dimensions evidenced by shifting of corresponding peaks on lower side. Furthermore, reactively sintered compositions were free from pyrochlore phase ($Pb_2Sb_2O_7$) as the associated peaks were absent in the diffraction pattern[23,32,33].

3.2 Microstructural Analysis

Figure 2 is representative HRTEM of particle morphology of powder obtained by mechanical activation for 10 h (MA-10). Along with several distinct spherical particles, few aggregates were also noticed, as normally observed[34]. Average particle size (d_{50}) achieved is about 22 nm - 25 nm for this activation time. This shows that 10 h milling is sufficient for chemical reactions to take place among the constituent oxides along with reduction in particle size to nano-meter scale.

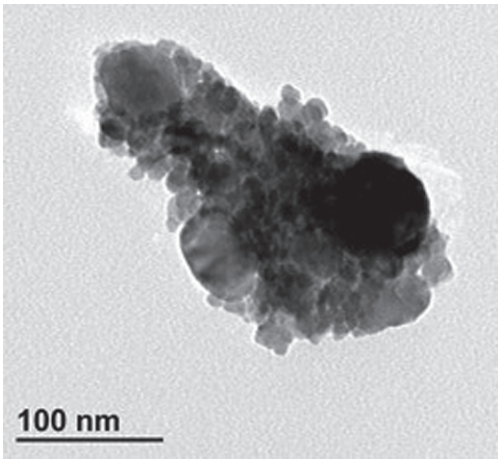

Figure 2. TEM of Nano-crystalline powder mechanically activated for 10 h (MA-10).

Figure 3 (a)-(e) shows the effect of mechanical activation on microstructure of the samples reactively sintered at 1220°C. The average grain size (d_{50}) was measured using liner intercept method. Increasing the activation time from 5 h to 10 h, d_{50} decreased and further it remained practically uniform till 30 h activation and increased noticeably at 40 h. Grains with assorted polygons accompanied by wide range of size distribution (≤12 μm) were observed at 5 h activation indicating insufficient time for activation and mixing (Fig. 3(a). As shown in Fig. 3(b), the grain morphology changed significantly on increasing the activation to 10 h. Closely packed, hexagonal shaped grains with straight edges were observed representing the complete grain growth. Size distribution of grains was also narrow. Reduction in porosity and porosity at triple grain point was observed which indicated better sinterability at 1220 °C for 10 h activation time. Increasing the activation time to 20 h and 30 h, grain size remained practically unchanged but compactness reduced which lead to appearance of few ovular shaped grains. Grain morphology drastically changed and

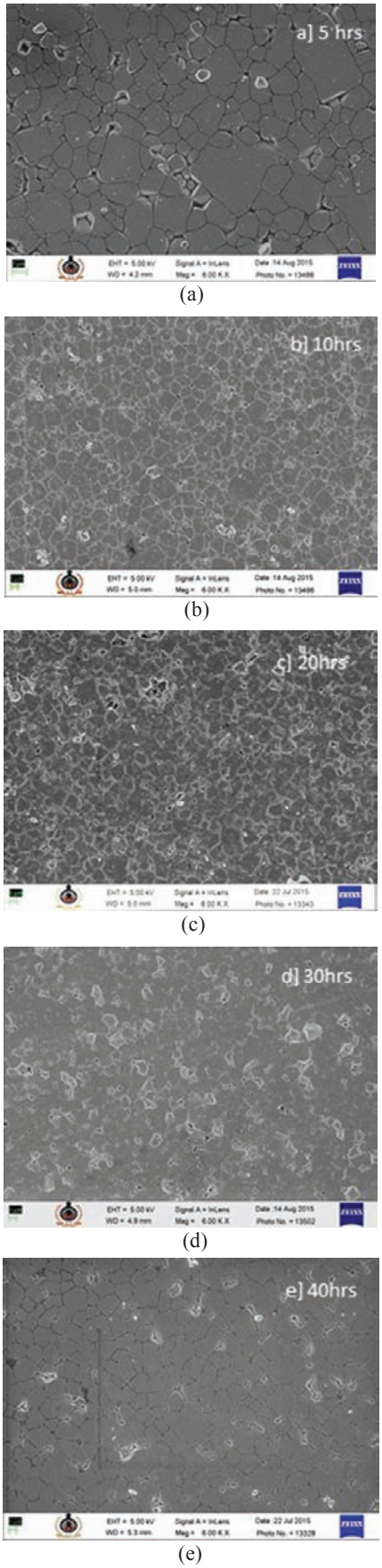

Figure 3. SEM of Reactively Sintered samples obtained from powders mechanically activated for (a) 5 h, (b) 10 h, (c) 20 h, (d) 30 h, and (e) 40 h.

multifarious sized and shaped grains were observed for 40 h activation, though microstructure is seen to be compact. The average grain size (d_{50}) measured was 3.46 µm, 1.65 µm, 1.67 µm, 1.76 µm, and 2.37 µm for the samples fabricated from powders mechanically activated for 5 h, 10 h, 20 h, 30 h, and 40 h respectively and reactively sintered at 1220 °C .

3.3 Piezoelectric Properties for Power Harvesting Applications

Effects of activation time on various dielectric and piezoelectric properties are listed in Table 1. Values of piezoelectric charge coefficient (d_{33}) obtained for 10 h of milling (449 pC/N) and 20 h of milling (457 pC/N) are improved and comparable. Superior values are attributed to the increased polarisibility and compact microstructure[22] having optimum grain size[35-38], as noticed in SEM micrographs for these activation durations. Increasing the activation time, it reduced to 229 pC/N (40 h). Piezoelectric voltage coefficient (g_{33}) and figure of Merit for power harvesting (FoM_{Ph})were calculated using general equations given in the literature. g_{33}values are influence by d_{33} and permittivity. Optimum value of g_{33}obtained at 10 h activation time attributed to better d_{33} and lower permittivity values (1585). Better value of d_{33} and optimum value of g_{33} resulted into optimum FoM_{Ph} [5,6,8,13,14] indicating the suitability of the composition activated for 10 h (MA-10) for power harvesting applications.

Table 1. Effect of Mechanical Activation time on various dielectric and piezoelectric properties

MA duration (h)	d_{33}(x10^{-12} C/N)	K_3^T	g_{33}(x10^{-3}m-V/N)	FoM_{PH} d_{33} * g_{33} (x10^{-12}V-m-C/N^2)
5	340	1592	24.1	8.2
10	449	1585	32.0	14.4
20	457	1762	29.3	13.4
30	420	1725	27.5	11.6
40	229	1437	18.0	4.1

3.4 Temperature Dependence and Stability of Properties

Figure 4 shows temperature dependence of permittivity and phase transition behavior investigated at 1 kHz for MA-10 samples. It was observed that, the permittivity remained almost unaltered till 150 °C. A small bump (T_{RT}) observed near 165 °C, refers to ferroelectric rhombohedral (F_R) to ferroelectric tetragonal (F_T) phase transition[39,40]. Further increasing the temperature, ferroelectric (F_E) to paraelectric (P_c) phase transition was observed at 290 °C indicated by sharp peak (T_c). It is interesting to note the excellent temperature stability of permittivity of the composition over the temperature range of -50 °C to 100 °C to which the aerospace / launch vehicles are generally subjected to during the operation.

3.5 Power Harvestability in Response to Random Vibrations

As shown in Fig. 5, components in the form of round discs (Φ 9.8 mm x thk 1.1 mm) were fixed on fixture using

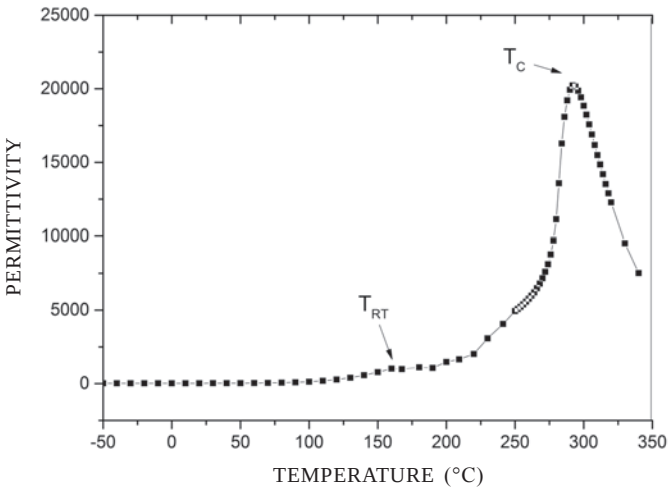

Figure 4. Temperature dependence of permittivity and phase transition behaviour.

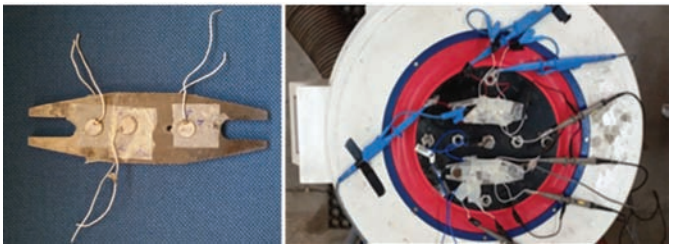

Figure 5. Fixture with components and vibration bench.

petro-wax (PCB Piezotronics) and the fixture was mounted by steel bolts on vibration bench.

Power spectrum density (PSD) values of random vibrations of aerospace vehicles along Z-axis as recorded by Manoj[28], *et.al*. were used as input to MA-10 piezo discs in our experimental work (Fig. 6). Components were allowed to freely vibrate along Z-axis along with the bench and the inertia of the disc is responsible for generator action in response to random vibrations.

Figure 7 shows the output voltage across load resistances between 1 kΩ - 7 kΩ of MA-10 piezo discs in response to

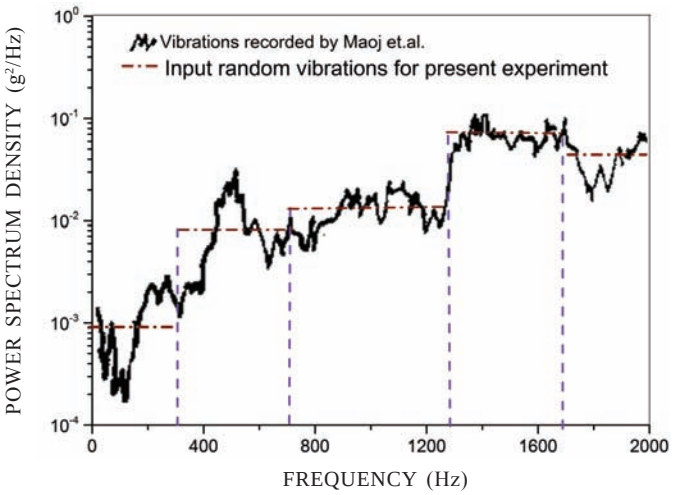

Figure 6. Random vibrations of aerospace vehicles along Z-axis[28].

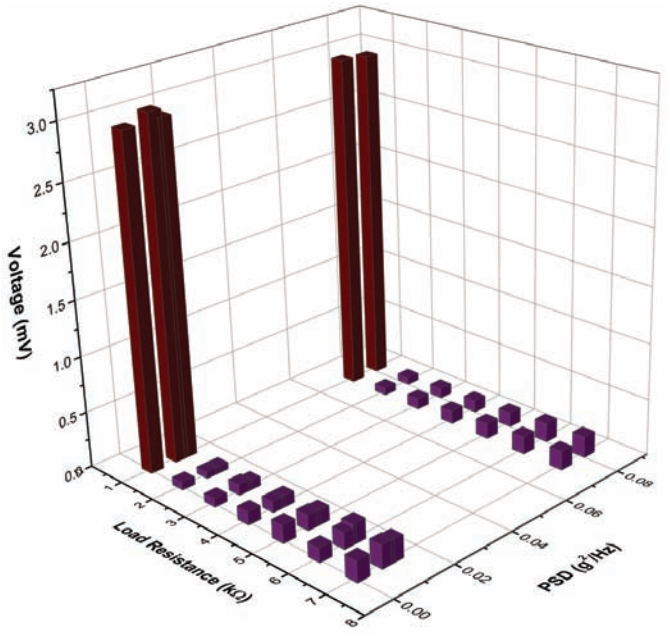

Figure 7. Voltage output at random vibrations in terms of PSD and load resistance.

random vibrations in terms of PSD. Maximum output voltage was obtained at 1 kΩ load resistance for the entire range of random vibrations applied in the experiment. Maximum output at this resistance is attributed to the matching of electrical impedance[41-44] of MA-10 piezo discs under the present experimental conditions. Moreover, the excellent uniformity of the output voltage (2.98 ± 0.04 mV) was observed. However the electrical output can be improved substantially by converting the components into vibration based devices like bimorph type cantilever modelled with the help of FEA software.

4. CONCLUSIONS

Pyrochlore free, $Pb_{0.98}La_{0.02}(NiSb)_{0.05}[(Zr_{0.52}Ti_{0.48})_{0.995}]_{0.95}O_3$ [La-PNS-PZT] composition, suitable for power harvesting has been synthesised using mechanochemical activation route. Progressive perovskite phase formation during mechanical activation and reactive sintering, analysed from XRD data, indicated the noticeable evidence of formation of perovskite phase after 10 h of activation and its completion during reactive sintering. HRTEM images shows the evidence of nano-structured particle size of the composition. Microstructural studies of samples carried out by FESEM indicated the compact microstructure for 10 h activation which resulted in optimum power harvesting piezoelectric properties accompanied by excellent stability of permittivity upto 100 °C. The electrical output evaluated in response to simulated random vibrations of aerospace vehicles at various power spectrum density values, measures at 3.0 mV output across the matched load resistance of 1 kΩ indicated suitability of composition for harvesting the power from vibrations of aerospace vehicles .

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