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Featured Letter

# Energy harvesting characteristic in piezoelectric nanoceramics with high mechanical property

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ABSTRACT

In this work, PZN–PZT piezoelectric nanoceramics were fabricated by SPS of nanocrystalline powders. It was found that Mn-doped nanoceramic possessed not only high mechanical properties, but also high $FOM_{off}$. Under high acceleration of 70 $m/s^2$, Mn-doped PZN–PZT harvester can still work properly without damage, and the output power density is as high as $162 \times 10^{-3}$ μW/$mm^3$. This research shows the Mn-doped nanoceramic having the potential application for building multi-layer micro-piezoelectric energy harvester.



## 1. Introduction

Piezoelectric energy harvesters can convert the vibration energy in the environment into electrical energy for clean power generation, which is a hot research topic in the field of new energy [1,2]. The multi-layer piezoelectric energy harvester, which has several layers of piezoelectric material positioned one over the other on both sides of the passive substructure, can significantly increase power generation in comparison with ordinary single-layer piezoelectric energy harvester [3,4]. In order to meet the miniaturization of multi-layer piezoelectric energy harvester, the key is building high-quality nanocrystalline ceramics, but the related study is rare, partly due to the severe deterioration of piezoelectric properties at the nanoscale [5,6].

Previously, our work demonstrated that submicron-grained Mn-doped PZN–PZT ceramics prepared using conventional ceramic processes have good piezoelectric performance, and the cantilever-type piezoelectric energy harvester made of this material can work normally even at high acceleration of 50 $m/s^2$ [7]. In this work, in order to extend the energy harvesting studies to nanoscale, we have chosen Mn-doped PZN–PZT as target system and prepared its nanoceramic form by SPS of nanocrystalline powders. The results demonstrated that the Mn-doped nanoceramic not only possessed high mechanical properties, but also exhibited favorable energy harvesting characteristic in the mode of the cantilever-type energy harvester, making this piezoelectric nanoceramic very suitable for application in new generation multi-layer harvester.

## 2. Experimental

Nanocrystalline 0.5 wt% $MnO_2$-doped $0.2Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.8Pb(Zr_{0.5}Ti_{0.5})O_3$ powder was synthesized from a mixture of $Pb_3O_4$, $ZrO_2$, $TiO_2$, ZnO, $Nb_2O_5$ and $MnO_2$, using high-energy ball milling system (Fritsch GmbH, Idar-Oberstein, Germany) [7]. After that, the nanoceramic was produced via SPS (SPS-3.20 MK-V, Sumitomo Coal Mining Co., Ltd., Tokyo, Japan) and heated at 800 °C for 30 s under 50 MPa. For comparison, the undoped PZN–PZT nanoceramic has also been prepared by the same process route.

The microstructure was detected by scanning electron microscope (S4800; Hitachi, Tokyo, Japan). Vickers indentation hardness $H_v$ was carried on a digital micro hardness tester (HXD-1000TMC/LCD, Taiming Inc., Shanghai, China) using a load of 9.8 N for 10 s, and the fracture toughness ($K_{IC}$) was calculated using the following equation [8]:

$$K_{IC} = \frac{0.0624P}{d \times l^{1/2}} \quad (1)$$

where $P$ is the load, $d$ is the diagonal length of the indentation, and $l$ is the crack's vertical length measured from the tip of indentation.

The detailed testing methods for electrical properties were described elsewhere [9]. The experimental setup for measuring the power generation characteristic and the detailed schematic diagram of cantilever-type harvester were given in Fig. S1 [10]. The test conditions are as follows: the resonance frequency is 88

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Hz, the acceleration is 0–70 $m/s^2$, and the load resistance is 0–3000 kΩ.

## 3. Results and discussions

The SEM micrographs of undoped and Mn-doped PZT–PZN ceramics were present in Fig. 1(a) and (b), respectively. Both specimens present the dense microstructures and the measured relative densities were above 98% by Archimedes method. In comparison with an average grain size of 95 nm for undoped PZT–PZN, the Mn doped specimen presents relatively lower size of 80 nm. Moreover, XRD patterns of undoped and doped specimens were present in Fig. S2. Both samples were pure perovskite phases and no second phase was found within the detection limit.

In order to apply to piezoelectric energy harvesters, piezoelectric ceramics need to have a high transduction coefficient ($d \times g$) to obtain a high energy density. Furthermore, the dielectric loss should also be considered because the performance of an energy harvester is affected by the electrical damping of piezoelectric ceramics. Therefore, the figure of merit in the off-resonance condition ($FOM_{off}$) for energy harvesters can be illustrated by the following formula, as suggested by Priya *et. al* [11]:

$$FOM_{off} = \frac{d \times g}{\tan\delta} = \frac{d^2}{\varepsilon_0 \times \varepsilon_r \times \tan\delta} \quad (2)$$

where $d$ is the piezoelectric charge constant, $g$ is the piezoelectric voltage coefficient, tan$\delta$ is the dielectric loss, $\varepsilon_0$ is the vacuum dielectric constant and $\varepsilon_r$ is the relative dielectric constant.

Fig. 1(c) gives the comparison of dielectric and piezoelectric properties between undoped and Mn-doped PZT–PZN nanoceramics. As can be seen, manganese doping reduces the $\varepsilon_r$, tan$\delta$ and $d_{33}$, simultaneously. This phenomenon can be attributed to the so-called "acceptor doping effect" as manganese doping induced the formation of oxygen vacancy, which pinned domain wall motion, resulting in decrease of $\varepsilon_r$, tan$\delta$ and $d_{33}$ [12]. However, it should be noted that the decrease in $\varepsilon_r$ after doping is small, but the decrease in tan$\delta$ is far greater than the $d_{33}$. This trade-off is "worth the price" and conducive to a significant enhancement of the $FOM_{off}$.

On the other hand, mechanical test was carried out for nanoceramics and the results are shown in Fig. 2. It can be found that regardless of whether doped or not, the nanoceramics exhibit excellent mechanical properties, i.e. the $H_v$ was 6.3–6.5 GPa and $K_{IC}$ was 1.8–2.2 $MPa{\cdot}m^{1/2}$, which are distinctly larger than the reported values of submicron-grained ceramics (The reference data are added in Fig. 2 for comparison) [13–15]. As grain boundaries are energy barriers to crack growth, the smaller the grain size, the higher the grain boundary volume content, the greater the difficulty of crack propagation [16]. Therefore, compared with the coarse-grained ceramics, nanoceramics have more excellent mechanical properties.

In order to evaluate the power generation characteristics of nanoceramics, doped and undoped materials of the same size were fabricated as cantilever-type piezoelectric energy harvesters. Fig. 3 (a) shows the variation of the output voltage with time under cyclic loading with the sine wave modes, and the measurements were performed at an acceleration of 10 $m/s^2$. The output voltage value of Mn-doped PZN–PZT harvester was superior to undoped harvester (peak-to-peak voltage of 3.60 V and 2.16 V, respectively). Meanwhile, as seen in Fig. 3 (b), at optimal load resistance, the output power density ($5.22 \times 10^{-3}$ $\mu W/mm^3$) of the Mn-doped PZT–PZN harvester was much higher than that ($2.27 \times 10^{-3}$ $\mu W/mm^3$) of undoped harvester. Moreover, taking into account the excellent mechanical properties of nanoceramics, we further tested the output voltage and output power density of two types of energy harvesters under strong acceleration excitation and the results were shown in Fig. 3(c) and (d). As can be seen, both energy harvesters can work properly without damage under high acceleration excitation. Especially at accelerations of up to 70 $m/s^2$, the temperature rise of the device is less than 2 °C after 30 min of harvesters operation. However, special attention needs to be paid here that compared with undoped counterpart, Mn-doped PZN–PZT energy harvester can generate very large output voltage and output power density. It is believed that manganese doping plays important roles in increasing $FOM_{off}$ and reducing mechanical loss, which are the main reason responsible for the large increase in energy harvesting characteristics at high acceleration excitation. At 70 $m/s^2$, the generated power density from the Mn-doped PZN–PZT harvester reaches the maximum values of $162 \times 10^{-3}$ $\mu W/mm^3$, which is about 8 times that of undoped counterpart and can successfully light up

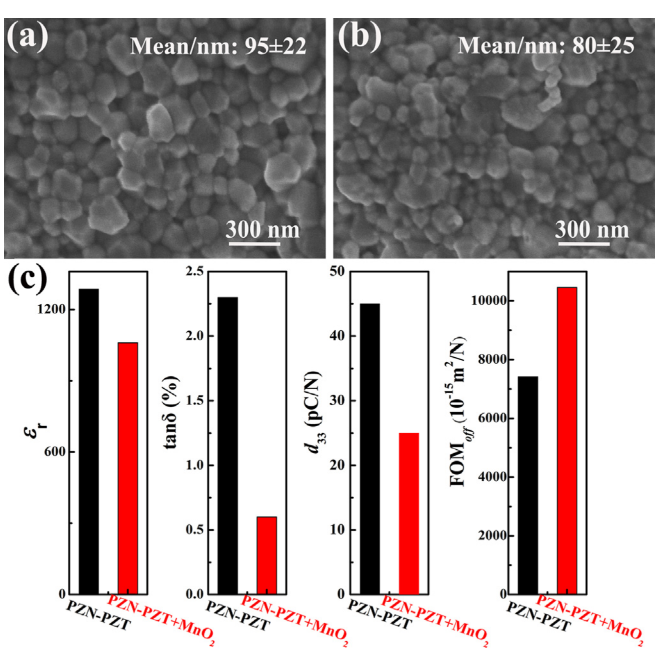


**Fig.1.** SEM micrographs of (a) undoped nanoceramic and (b) Mn-doped PZN–PZT nanoceramic, (c) $\varepsilon_r$, tan$\delta$, $d_{33}$ and $FOM_{off}$ values for undoped and Mn-doped PZN–PZT nanoceramics.

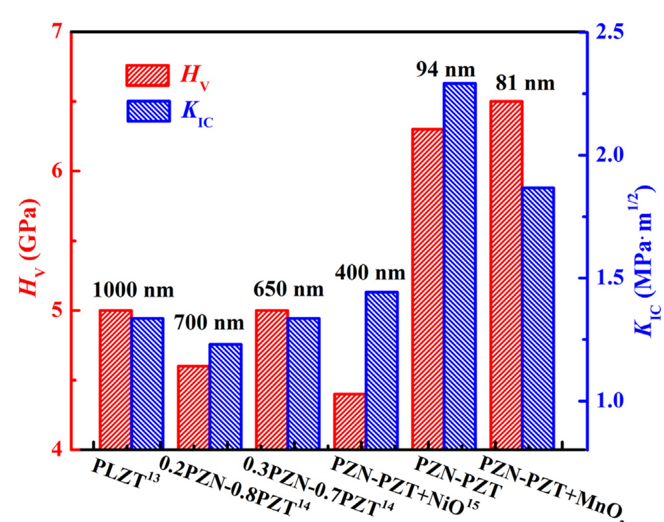


**Fig.2.** Histograms of the $H_v$ and $K_{IC}$ values of PZN–PZT nanoceramics with and without Mn doping. The data of coarse-grained ceramics are added as reference.